Vibrational structures in electron–CO$_2$ scattering below the $^2\Pi_u$ shape resonance

Michael Allan

Department of Chemistry, University of Fribourg, Ch. du Musée 9, CH-1700 Fribourg, Switzerland

Abstract

Structures of vibrational origin were discovered in vibrationally inelastic electron–CO$_2$ cross sections in the energy range 0.4–0.9 eV, well below the $^2\Pi_u$ shape resonance. They appear in the excitation of higher vibrational levels, in particular the highest members of the Fermi polyads of the type $(n, 2m, 0)$ with $n + m = 2$–4. The lowest two structures, at 0.445 and 0.525 eV, are narrow; higher-lying structures are broader and boomerang-like. The structures are absent when the antisymmetric stretch is co-excited. The structures are interpreted in terms of a wavepacket of the nuclei reflected from a potential surface of the CO$_2^-$ anion in a bent and stretched geometry. A state emerging from the virtual state upon bending and stretching and the state resulting from bending the $^2\Pi_u$ shape resonance are discussed as possibly being responsible for the structures.

1. Introduction

Vibrational excitation in CO$_2$ has two distinct energy ranges: a $^2\Pi_u$ shape resonance around 3.6 eV, where boomerang structures have long been known (Boness and Schulz 1974), and a virtual state below 2 eV (Morrison 1982, Herzenberg 1984, Kochem *et al* 1985, Estrada and Domcke 1985, Morgan 1998, Rescigno *et al* 1999, Mazevet *et al* 2001, Field *et al* 2001). The virtual state causes dramatic enhancement of the cross section near threshold ('threshold peak') for the excitation of the symmetric stretch vibration (100), Fermi-coupled with two quanta of the bending vibration (02^{0}0) (Kochem *et al* 1985, Field *et al* 1991, Allan 2001a). The cross sections for the excitation of the infrared active fundamental vibrations, (010) and (001), also exhibit threshold peaks, but these can be ascribed, at least to a large degree, to direct dipole scattering (Kochem *et al* 1985). Pronounced selectivity was observed in the excitation of the Fermi-coupled vibrations {(10^{0}0), (02^{0}0)} in the virtual state range (Antoni *et al* 1986, Allan 2001a). Selectivity in the excitation of the Fermi-coupled vibrations was also observed in the shape resonance region (Johnstone *et al* 1995, Kitajima *et al* 2000, Allan 2001a), which is not the primary region of interest of this study, however.

In contrast to the $^2\Pi_u$ shape resonance region, the cross sections reported so far in the virtual state region did not exhibit structures of vibrational origin. This letter reports structures of vibrational origin in the virtual state region of CO_2. They appear in the excitation of certain higher-lying Fermi-coupled vibrations involving symmetric stretch and bending (Allan 2002).

2. Experiment

The measurements were performed using a spectrometer with hemispherical analysers described by Allan (1992, 1995). The response function of the spectrometer at very low energies has recently been improved by adding more degrees of freedom in compensating residual electric fields in the collision region. The resolution of the instrument has also been improved by using rectangular apertures to define the pupil, providing a ribbon-shaped beam in the analysers (Allan 2001a). In order to gain sensitivity, the resolution of the spectrometer was reduced in this study to 11 meV for recording the energy-loss spectrum, and to 16 meV for recording the cross sections as a function of energy (both values refer to fwhm in the energy-loss mode). The resolution in the incident electron beam was consequently about $16\,\mathrm{meV}/\sqrt{2} \cong 11\,\mathrm{meV}$ in the 'energy dependence' spectra. The energy of the incident beam was calibrated on the 19.366 eV ^{2}S resonance in helium and is accurate to within ±20 meV. The analyser response function was determined on the elastic scattering in helium. The sample inlet nozzle had a diameter of 0.25 mm and was kept at $\sim30\,^\circ$C during the measurements.

Absolute value of the elastic cross section was determined by comparison with the elastic cross section of helium of Nesbet (1979) at 0.3 and at 3 eV using the relative flow method. The inelastic cross sections in the left part of figure 1 were normalized to the elastic cross section and are accurate to within $\pm30\%$ (less accurate within the first 200 meV above threshold) (Allan 2001a). The present cross sections for the higher-lying vibrational states were normalized to the older inelastic data at 50 meV above threshold using the relative band intensities in an energy-loss spectrum. The accuracy of the present absolute values is adversely affected by the rapid variation of the cross sections 50 meV above threshold and the difficulty of controlling the response function very close to threshold. The absolute values for the higher vibrational levels are consequently estimated to be reliable to within a factor of two. The present experiments were performed at a range of pressures to ascertain that the observed structures are not due to clusters, where vibrational Feshbach resonances have recently been observed by Leber *et al* (2000).

3. Results

Figure 1 shows an overview of the cross sections in CO_2. The left part shows the elastic cross section and the inelastic cross sections for the excitation of the fundamental vibrations (the (10^00) state being in a Fermi resonance with (02^00)). The elastic and all inelastic cross sections with the exception of the lower member of the Fermi dyad (FR_I) have an intense threshold peak. These peaks have been attributed to a virtual resonance for the elastic cross section (see the citations given in the introduction) and for the upper member of the Fermi dyad (FR_{II}) (Kochem *et al* 1985, Estrada and Domcke 1985). The threshold peaks in the (010) and (001) cross section have been interpreted as mainly due to direct dipole excitation (Kochem *et al* 1985). The cross sections within the threshold peak are, in contrast to those in, for example, hydrogen halides or CS_2 (Allan 2001c), structureless.

Vibrational structures in cross sections are often more pronounced in the excitation of higher overtone vibrations, which probe the potential of the negative ion at larger internuclear
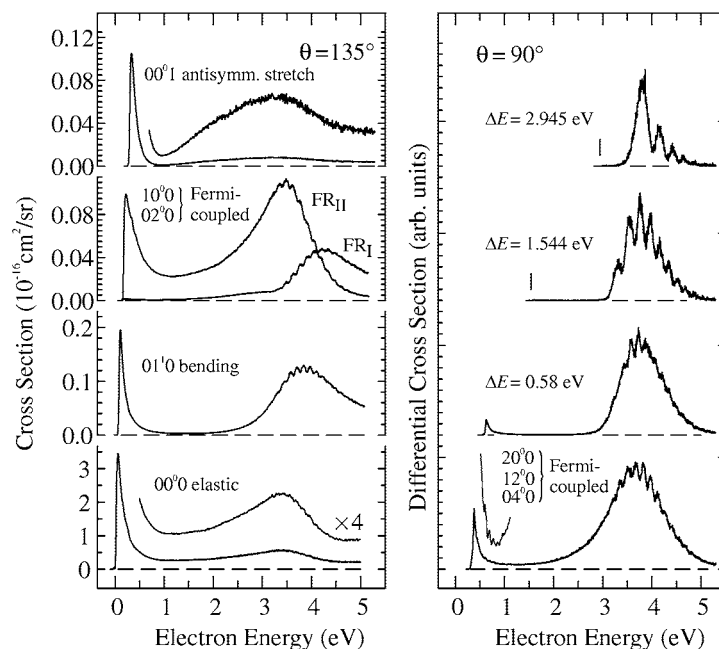
Figure 1. Overview of the elastic and vibrationally inelastic cross sections in CO_2. Reproduced from Allan (2002).

distances, where autodetachment widths are narrower or where the anion curve even lies below that of the neutral molecule. A dramatic example is H_2, with no structure in the $v = 1$ and 2 cross sections, and deep structure for $v \geqslant 4$ (Mündel *et al* 1985, Allan 1985). This rule is confirmed by the CO_2 cross sections in the $^2\Pi_u$ shape resonance region, where structures become deeper with increasing vibrational level. Applying this strategy to the search for structures in the virtual state region in CO_2 is hindered by the fact that the cross sections at threshold drop rapidly for higher final channels, as illustrated in the right part of figure 1. A weak threshold peak is observed only for few relatively low-lying vibrational overtones. A preliminary observation of weak undulations on one of these has been reported (Allan 2002) and is reproduced in figure 1.

This work aims at investigating these undulations in more detail. In a first step an energy loss spectrum has been recorded at a low residual energy (figure 2) to identify the vibrations which are excited close to threshold with measurable intensities. Three of the prominent overtone bands in the expanded sections of the spectrum form an apparent progression with a spacing equal to the energy of the upper member of the $\{(10^00), (02^00)\}$ Fermi dyad. They are the topmost members of the Fermi polyads $\{(n, 2m^0, 0)\}$ with $n + m = 2$–4 (Chedin 1979, Requena *et al* 1993). This shows that the selectivity found for the $\{(10^00), (02^00)\}$ Fermi dyad is continued to the higher polyads; only the highest members are excited by the virtual state. In addition, the upper member of the $\{(11^10), (03^10)\}$ dyad and several states including the excitation of the antisymmetric stretch vibration ((011), the upper member of the $\{(10^01), (02^01)\}$ dyad and the overtone (002)) are observed.

The cross sections for exciting the top members of the $\{(n, 2m^0, 0)\}$ polyads are shown as a function of the incident electron energy in figure 3. Structures of varying widths and depths are observed in all the cross sections and their properties can be characterized as follows.
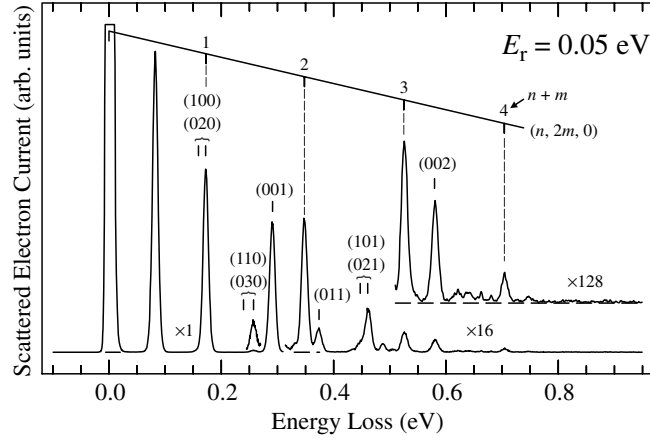
Figure 2. Electron energy loss spectrum recorded 0.05 eV above threshold. The grid above the spectrum indicates the highest members of the Fermi polyads $\{(n, 2m, 0)\}$ with $n + m$ indicating which vibrational levels are excited close to threshold.
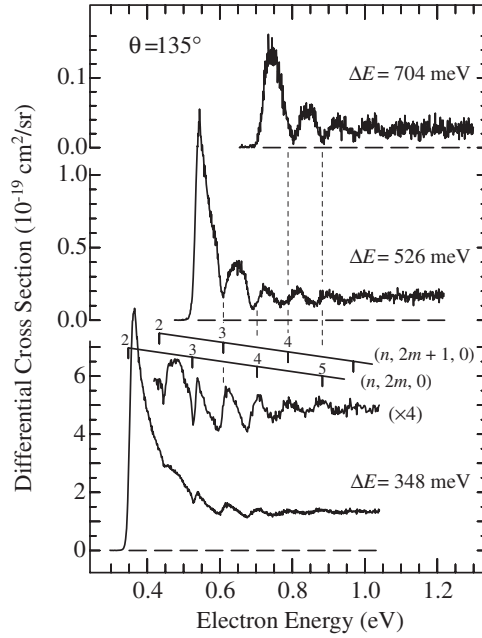

Figure 3. Cross sections for exciting the highest members of the Fermi polyads $\{(n, 2m^0, 0)\}$ with (from bottom to top) $n + m = 2$–4. The bottom spectrum is also shown with smooth curved mean line subtracted and vertically expanded to enhance the visibility of the structures. The grids above the bottom spectrum show the thresholds for exciting the highest members of the polyads $\{(n, 2m^0, 0)\}$ and $\{(n, 2m + 1^1, 0)\}$, with the sums $n + m$ given.

- The structures become deeper with higher-lying final channels. This corresponds to the general trend described above.

- The first two structures are very narrow, with widths comparable to instrumental resolution; the higher-lying structures become progressively broader.
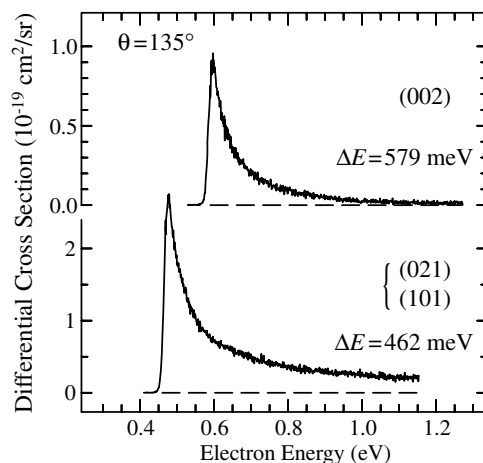
Figure 4. Cross sections for exciting overtone and combination vibrations containing the asymmetric stretch.

- The first two narrow structures coincide, within the confidence limit of the energy scale calibration, with vibrational thresholds for the topmost members of the $\{(n, 2m+1^1, 0)\}$, $n + m = 2$, and $\{(n, 2m^0, 0)\}$, $n + m = 3$ polyads. The higher-lying structures, for example $\{(n, 2m^0, 0)\}$, $n + m = 4$, lie slightly below the threshold, and the highest, oscillatory, structures do not have clear relation to particular thresholds. These observations indicate that the low-lying structures are either cusps or vibrational Feshbach resonances lying very close to the parent vibrational level. The higher-lying structures are vibrational Feshbach resonances with gradually increasing width, which lie gradually deeper below the parent levels.
- The highest, oscillatory, structures have their peaks and dips at different energies in the different final channels, a characteristic of boomerang structures. A dip in one channel generally corresponds approximately (but not exactly) to a peak in the next channel and vice versa.

Figure 4 shows the cross sections for exciting three vibrational states containing the antisymmetric stretch. None of the curves has any discernible structure—the antisymmetric stretch quenches the vibrational structures in the cross sections.

4. Discussion

Figure 1 shows that the well known boomerang structures in the $^2\Pi_u$ shape resonance region disappear below about 3.22 eV, and the $^2\Pi_u$ band is structureless below this energy. The structures reported here are separated by a substantial energy gap from the 'old' structures in the $^2\Pi_u$ region, indicating that they have a different origin.

Vibrational structures in cross sections are generally a sign of a nuclear wavepacket being reflected by a potential surface of a negative ion. Multiple reflections result in narrow structures; an essentially single reflection followed by an annihilation of the wavepacket at the inner turning point gives rise to broad 'boomerang' structures (Herzenberg 1984). The vibrational structures thus indicate that, within the reach of the nuclear wavepacket, there is a section of negative ion potential surface (or curve for diatomics) where the autodetachment width is narrow (as in N_2) or the anion is even electronically bound (as in HF). The structures observed
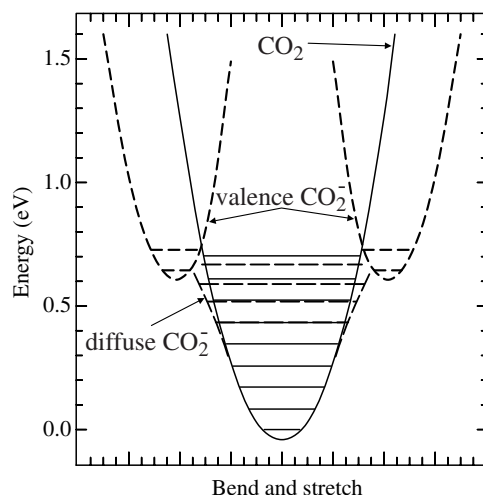
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Figure 5. Hypothetical potential curves for CO_2 and CO_2^-. The horizontal coordinate symbolizes simultaneous symmetric stretch and bending distortions, corresponding schematically to the motion of the nuclei in the upper Fermi coupled states. The potential curve of the valence state of CO_2^- is drawn to comply approximately with an adiabatic electron affinity of -0.65 eV. This curve would have to be about 0.3 eV lower if it were to explain the structures reported here. An alternative explanation would be a diffuse state of CO_2^- supporting vibrational Feshbach resonances, indicated by long-dashed curves.

here for CO_2 are strikingly similar to those observed in HF (Knoth *et al* 1989, Sergenton *et al* 2000, Allan 2001b). The similarity spans nearly all the properties itemized in the preceding section, suggesting that similar physics is likely to govern the motion of the nuclei in both cases, although the physical mechanism of the binding of the electron for a distorted molecule may differ. The similarities include the shapes and narrow widths of the structures at low energies, the fact that the structures drop measurably below the parent vibrational levels at higher energies, interpreted as a proof of vibrational Feshbach resonances by Knoth *et al* in HF, and the increasing width and depth of the structures at higher energies and higher final channels.

The question of the nature of the negative ion state must then be posed. The discussion is illustrated by figure 5. It was recognized early (Krauss and Neumann 1972) that the lower branch of the potential curve of the $^2\Pi_u$ valence state of the anion, $^2A_1$, drops below the curve of the neutral CO_2 upon bending and stretching. The long-lived ($\sim 10^{-5}$ s) metastable state of CO_2^-, observed in a mass spectrometer by Cooper and Compton (1972), is assumed to correspond to the lowest vibrational state on this potential surface. The metastable vibrational levels of the bent and stretched valence CO_2^- state could communicate by tunnelling with the low-energy scattering process dominated by the virtual state and the coherent superposition of the two processes could be responsible for the observed structures. The process would resemble the 'outer well resonances' postulated theoretically and confirmed experimentally in vibrational excitation of HCl (Allan *et al* 2000).

Two arguments speak against this 'valence state' explanation, though. The $^2A_1$ state of CO_2^- is generally thought to be at higher energies. The adiabatic electron affinity of CO_2 has been measured as -0.4 ± 0.2 (Cooper and Compton 1973) and -0.6 ± 0.2 eV (Compton *et al* 1975). A recent calculation at the CCSD(T) level (coupled-cluster method with all singles, doubles, and non-iterative inclusion of triple excitations) yielded -0.67 eV (Gutsev *et al* 1998).

The lowest structure (a dip) in the present study is observed at 0.445 ± 0.02 eV. This structure is unlikely to be the lowest vibrational level of the valence anion state, however, because the lifetime of the metastable CO_2^-, measured by Cooper and Compton (1972) to be around 10^{-5} s, indicates an energy width far below 1 meV, too narrow to be observed in the present experiment. The ground vibrational level of the metastable CO_2^- would thus have to be at least one (bending) vibrational spacing below the lowest structure in the present spectra, that is, at or below 0.36 eV. This value is within the error limit of the first measurement of the adiabatic electron affinity, but below the value given by the second measurement and the theory. The second argument is that the near coincidence of the two lowest structures with the vibrational thresholds would have to be accidental. Such a coincidence cannot be excluded, but is not very probable. A comparison of the vibrational frequencies of the $^2A_1$ bent valence state of CO_2^- and the spacing of the present structure could, in principle, also be used as a test of the valence state hypothesis. The large discrepancy between the experimental value of 105 meV (measured in a matrix by Hartman and Hisatsune (1966)) and the calculated value of 84 meV (Gutsev *et al* 1998) prevents conclusions, however. The calculated value is in good agreement with our observed spacing, but it is also nearly equal to the bending vibration spacing of the neutral molecule.

A second candidate for the low-lying CO_2^- state emerges when one assumes that the virtual state, described as a 'state on the verge of being born', becomes 'truly born' at a bent and stretched geometry of the CO_2. The observed structure would be a consequence of the reflection of the nuclear wavepacket on this potential surface. This state would also be of $^2A_1$ symmetry but would consist of a very diffuse electron cloud bound to the bent and stretched CO_2 by a combination of dipole, quadrupole and polarization potentials. Gutsev *et al* (1998) calculated a dipole moment of 0.9 D for bent CO_2 (equilibrium geometry of CO_2^-), too small to sustain a dipole-bound state. Nooijen and Bartlett (1995) concluded that no weakly bound (excited) state of CO_2^- is found at the equilibrium geometry of the valence CO_2^- state. Gutsev *et al* calculated a quadrupole moment of 3.27 au (in agreement with experiment) for linear CO_2, however, which is more than the minimum value of 2.6 au proposed by Prasad *et al* (1989, 1991) to be required for a quadrupole bound state (although this value of the critical quadrupole moment may be too low). It thus appears that the existence of a weakly electronically bound CO_2^- surface at bent and stretched geometries cannot be positively excluded on theoretical grounds at present. What is a virtual state at a linear geometry, that is, a state nearly bound, mainly by polarization, could become an electronically bound state at a bent and stretched geometry through the additional attraction of the dipole moment or even increased polarizability. Such a 'diffuse state' would support vibrational Feshbach resonances and boomerang structures and remains a viable candidate for the explanation of the structures reported here. The valence and the diffuse states have the same symmetry and would develop an avoided crossing and a conical intersection similar to that between Rydberg and valence states of neutral molecules. A conical intersection of this type has recently been proposed in a study using an analytically solvable model of electron–CO_2 scattering by Vanroose *et al* (2002). A similar situation has been discussed by Sommerfeld (2002) in a nitromethane anion. The conical intersection would have to be quite far from the bottom of the valence state potential to explain the long-lived CO_2^- anion observed by Cooper and Compton (1972).

Finally, it is interesting to compare the present structures to those reported by Leber *et al* (2000) in dissociative electron attachment to CO_2 clusters. They observed structures below the (010) and the $\{(1, 0^00), (02^00)\}$ thresholds, with the difference that a structure was observed for each member of the latter Fermi dyad in their spectra, whereas in the present study a structure is observed only for the topmost members of the Fermi polyads.

5. Conclusions

Structures of vibrational origin—vibrational Feshbach resonances and boomerang oscillations—were observed in electron–CO_2 scattering at low energies, where cross sections are dominated by a virtual state. The structures appear in the cross sections for excitation of higher-lying Fermi-coupled vibrations involving symmetric stretch and bending. They are taken as an indication of a low-lying potential surface of CO_2^-, lying below the potential surface of the neutral CO_2 at a bent and stretched geometry. Two candidates for the CO_2^- state implied are considered:

(i) the well known valence state which results when CO_2^- in the $^2\Pi_u$ shape resonance state is stabilized by bending, and
(ii) a state where a diffuse electron cloud is weakly electronically bound to a bent CO_2 by a combination of dipole, quadrupole and polarization forces.

Both explanations have problems. The former would require that the valence state lies lower (i.e., that the adiabatic electron affinity of CO_2 is larger) than generally assumed. The latter explanation appears more viable, but has the problem that calculations did not yet find the diffuse weakly bound state. Further theoretical effort will be required to resolve these problems.

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