

## Selectivity in the Excitation of Fermi-Coupled Vibrations in CO<sub>2</sub> by Impact of Slow Electrons

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Improvement of resolution of a gas phase hemispherical electron spectrometer (to 7 meV FWHM) permitted separate measurements of the excitation of each member of the well known Fermi dyad in CO<sub>2</sub> by impact of slow electrons. Absolute differential cross sections at a scattering angle of 135° were measured as a function of electron energy. The excitation was found to be highly selective both via the <sup>2</sup>Π<sub>u</sub> shape resonance around 3.6 eV and via the virtual CO<sub>2</sub><sup>-</sup> state at low energy. The selectivity is surprising because both vibrational states ensuing from the Fermi resonance involve the same type of nuclear motion (bending and stretch) and excitation of both is symmetry allowed.

The interest in vibrational excitation by electron impact in the gas phase is motivated by the intriguing ultrafast phenomena which it involves and by the key role which it plays in technological and natural plasmas. The excitation of the individual normal modes of polyatomic molecules has been found to be highly selective, as a result of symmetry selection rules [1,2] and the fact that the intensity of the allowed vibrational transitions depends on the force field exerted on the nuclei by the negative ion resonances mediating much of the vibrational excitation [3,4]. Very little is known about the selectivity of excitation of vibrations coupled by Fermi resonances, however, because the resulting states are too closely spaced to be resolved by electron energy-loss spectrometers, and only sums of the cross sections for the Fermi-coupled vibrational states could generally be measured so far.

A prototype example of Fermi coupling is found between one quantum of symmetric stretch (10<sup>0</sup>) and two quanta of bending (02<sup>0</sup>) in CO<sub>2</sub>, which are accidentally nearly degenerate. The coupling results in two vibrational states (a Fermi dyad) at 159 and 172 meV, which are nearly 50%–50% mixtures of bend and symmetric stretch [5–7]. These two states have already been partially resolved in electron scattering by Antoni *et al.* [8], who reported energy-loss spectra with a resolution of 11 meV and saw the Fermi dyad as broadened and asymmetric band profiles. Their energy-loss spectra recorded at fixed incident electron energies indicated a pronounced selectivity: only the upper member was excited at threshold while spectra recorded in the 3.6 eV shape resonance region showed both members, the upper being stronger.

The generally superior resolution of electron spectrometers for surface work recently permitted Krenzer *et al.* [9] to resolve the Fermi dyad for CO<sub>2</sub> adsorbed on a silver surface. (The electron spectrometers for surface work benefit from larger signal intensity due to a denser target, from the absence of Doppler and rotational broadening, and from cleaner surfaces of the electron optics under UHV conditions.) They reported energy-loss spectra recorded at fixed incident electron energies of 5 and 10 eV. The lower member of the dyad was found to dominate at both energies, in

contrast to the gas phase work, posing the question whether the excitation mechanism is different in the gas phase and for the adsorbed molecules.

CO<sub>2</sub> represents a particularly suitable system for the study of the selectivity, because it offers the possibility to investigate the excitation by two fundamentally different excitation mechanisms: a <sup>2</sup>Π<sub>u</sub> shape resonance around 3.6 eV [10] and a virtual state at energies near threshold [4,11–13]. (Electron scattering in CO<sub>2</sub> has been studied many times both experimentally and theoretically, and only a few representative citations can be given here.) The study of Fermi-coupled vibrations is further motivated by the fact that the selectivity indicated by the earlier work both in the gas phase and on a surface is surprising. It is not explained by the symmetry selection rules [1,2]—both members of the Fermi dyad have the σ<sub>g</sub> symmetry, and the excitation of both is thus symmetry allowed, via the <sup>2</sup>Π<sub>u</sub> shape resonance at 3.6 eV as well as via the Σ<sub>g</sub> virtual state at threshold. In addition, both members of the dyad contain the same types of nuclear motion (symmetric stretch and bending) and both may thus be expected to be excited to a comparable degree (by “intensity borrowing”) in a way similar to the excitation of both states in the Raman experiment [14], which has pointed out the phenomenon of the Fermi coupling in the first place [5].

This Letter reports a decisive improvement of resolution of a gas phase electron energy-loss spectrometer—currently around 7 meV—which reveals the Fermi dyad as separate peaks (Fig. 1). The improved resolution is combined with sufficient signal intensity, very low background, and with an analyzer response function controlled down to within 30 meV of threshold, permitting a separate recording of the cross section of each of the two Fermi-coupled states as a function of the electron energy. These excitation functions are indispensable for the experimental assessment of the selectivity.

The spectrometer [15,16] uses hemispherical electrostatic deflectors to analyze kinetic energies of electrons. The present improvement of resolution has been achieved mainly by the use of rectangular apertures (height:width about 2.5:1) defining the pupil, both in the monochromator

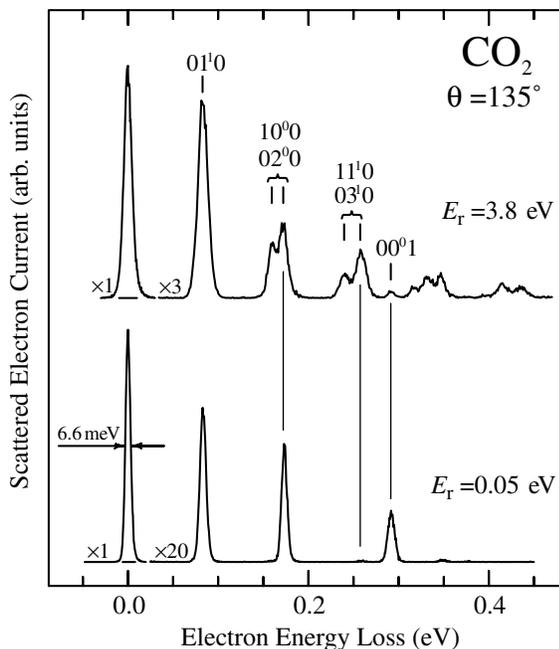


FIG. 1. Energy-loss spectra recorded very near threshold, with a residual energy  $E_r = 0.05$  eV (bottom), and in the  ${}^2\Pi_u$  resonance region (top).

and in the analyzer. They provide a flat, ribbonlike profile of the beams in the hemispherical analyzers, wide in the tangential direction where the aberrations are small, and thin in the radial direction where the aberrations are large. In comparison with the customary circular apertures the aberrations are reduced while keeping throughput reasonably high. A second important experimental aspect of the present work is that additional degrees of freedom in compensating residual electric fields in the collision region (a by-product of the recently installed [17] “magnetic angle changer”) substantially improved the response function at very low energies. Absolute values of the cross section were determined by comparison with the elastic cross section of helium [18] using the relative flow method. The sample inlet nozzle had a diameter of 0.25 mm and was kept at 40 °C during the measurements. The resulting 8% population of the  $(01^1_0)$  state has been taken into account in the determination of the absolute cross sections.

The present work investigates the excitation of the Fermi dyad as a function of incident electron energy at the large scattering angles of 90° and 135° where the virtual state contribution dominates over direct dipole excitation. The threshold energy-loss spectrum (lower curve in Fig. 1) reveals the excitation of the infrared active fundamental vibrations  $(01^1_0)$  and  $(00^0_1)$ , as well as the upper member of the Fermi dyad,  $\text{FR}_{\text{II}}$ . The excitation of the lower member of the Fermi dyad,  $\text{FR}_{\text{I}}$ , and of overtone and combination vibrations is very weak. The  ${}^2\Pi_u$  resonance (upper curve in Fig. 1) causes strong excitation of the  $(01^1_0)$  bending vibration and of both members of the Fermi dyad. The excitation of overtone and combination vibrations involving

bending and symmetric stretch (many of them also affected by Fermi resonances) is pronounced in the shape resonance region. The excitation of the antisymmetric stretch vibration  $(00^0_1)$  is relatively weak. (The larger peak widths in the upper spectrum of Fig. 1 are due to increased Doppler broadening at higher electron energies and to a more extensive rotational excitation.)

The principal result of the present study is shown in Fig. 2. It reveals striking differences between the cross sections for exciting the two Fermi-coupled states in *each* of the three energy regions into which the present experiment can be divided. In the threshold region below about 1 eV a prominent threshold peak is found for  $\text{FR}_{\text{II}}$ , but none for  $\text{FR}_{\text{I}}$ . Broad band is found for both cross sections in the shape resonance region above about 2.5 eV, but the bands peak at substantially different energies, around 3.5 eV for  $\text{FR}_{\text{II}}$ , around 4.2 eV for  $\text{FR}_{\text{I}}$ . The well known “boomerang” structure [4,10] is superimposed on the band in both cross sections. Finally in the intermediate region (at which no resonant mechanism has been postulated so far) the cross section is nearly zero for  $\text{FR}_{\text{I}}$ , but retains a substantial value for  $\text{FR}_{\text{II}}$ .

One may be tempted to assign the lower member of the dyad as predominantly bending  $(02^0_0)$ , and the upper member as predominantly symmetric stretch  $(10^0_0)$ , explaining the observed selectivity at threshold by the fact that the virtual state is evidently inefficient in exciting overtone vibrations in general, and only the fundamental of the symmetric stretch is excited at threshold. This explanation is, however, unacceptable in view of the firmly established strong mixing of the two normal vibrations by the Fermi resonance [6,7].

The discussion of the possible reasons of the selectivity will be started by considering the vibrational wave functions taken from the paper of Colbert and Sibert [7] and reproduced together with expanded spectra of the Fermi-coupled states in Fig. 3. They indicate that in the lower

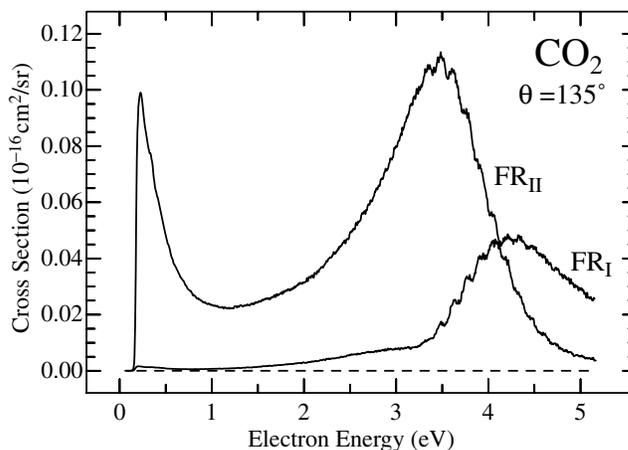


FIG. 2. Excitation functions of the two members of the Fermi dyad ( $\text{FR}_{\text{I}}$  and  $\text{FR}_{\text{II}}$ ), recorded at the energy losses of 0.159 and 0.172 eV, respectively.

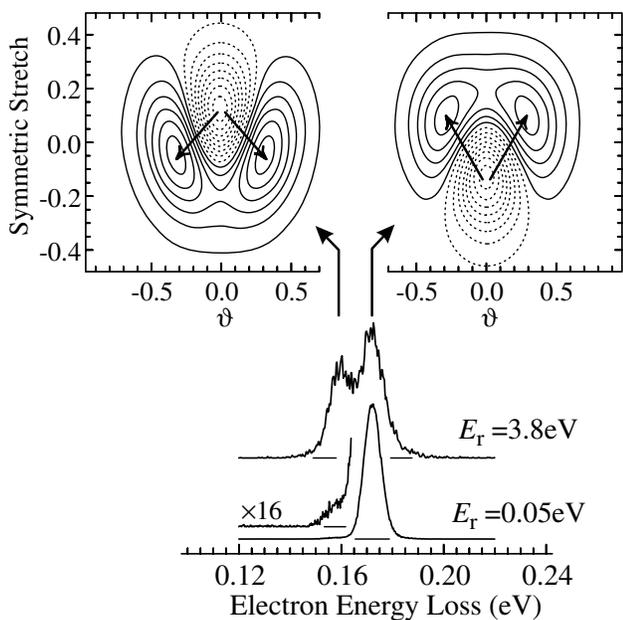


FIG. 3. Vibrational wave functions (from the paper of Colbert and Sibert [7]) of the two states of the Fermi dyad shown in the expanded spectra below (recorded at  $\theta = 90^\circ$ ). The wave functions are shown in a function of the bending and the symmetric stretch coordinates. The arrows on the wave functions indicate the direction of motion of the nuclei.

of the two Fermi-coupled states there is a large amplitude to find the molecule either stretched and nearly linear, or squeezed and bent. This means, in classical terms, that the molecule first stretches and straightens, then shrinks and bends. The relation is opposite for the upper of the two Fermi-coupled states, there is a large amplitude to find the molecule either stretched and bent or squeezed and nearly linear—classically speaking the molecule first stretches and bends, then shrinks and straightens. Stretching and bending occurs *out-of-phase* in FR<sub>I</sub> and *in-phase* in FR<sub>II</sub>.

Let us now consider the shape resonance region. The two components of the  $^2\Pi_u$  resonance split upon bending into the  $^2A_1$  and the  $^2B_2$  resonances [19]. The qualitative potential curves in Fig. 4 show that both components of the shape resonance are repulsive with respect to the symmetric stretch, whereas only the lower branch drops with bending. [The curves shown here are based on Hartree-Fock (HF) calculations with the 6-31G\* basis set. The total HF energy at various geometries is plotted for the neutral molecule, and the energies of the resonances are estimated at each geometry from the virtual orbital energies within the framework of the Koopmans theorem [20], using the empirical scaling relation of Ref. [21].] The effect of the lower branch is thus to impart, within a very short amount of time, an impulse in the direction of stretching and bending *simultaneously*, the correct direction to excite the upper, but not the lower, member of the Fermi dyad. This explains the lower energy of the band in the FR<sub>II</sub> cross section in Fig. 2. Similarly, the direction of the momentum

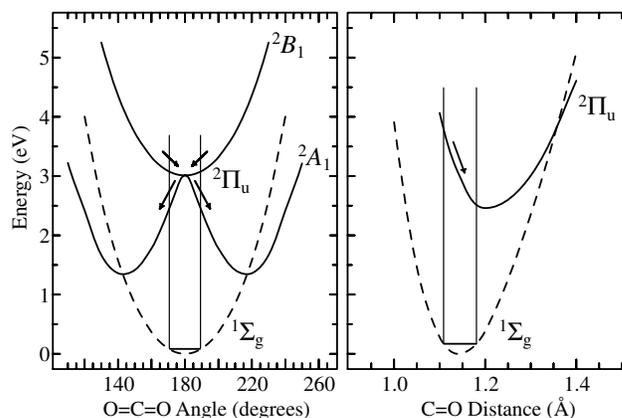


FIG. 4. Qualitative potential curves for  $\text{CO}_2$  (dashed) and  $\text{CO}_2^-$  (solid line) with respect to bending (left) and symmetric stretch (right). The arrows indicate in which directions the nuclei slide after the attachment of an electron.

applied to the nuclei by the upper branch of the potential fits the motion in the lower member of the Fermi dyad, explaining the higher energy of the band in the FR<sub>I</sub> cross section in Fig. 2. In quantum mechanical terms, the nuclear wave packet starts to move outwards along the symmetric stretch coordinate and simultaneously to widen and to split along the bending coordinate on the  $^2A_1$  branch of the potential during the short lifetime of the resonance (pictorial views were given by Kazansky and Sergeeva [22]). The wave packet distorted in this way overlaps well with the final wave function on the right side of Fig. 3 but poorly with the wave function on the left. The nuclear wave packet on the upper branch of the potential moves outward along the symmetric stretch coordinate, but does not spread along the bending coordinate, resulting in a perturbed wave packet overlapping well with the final wave function of the lower but not the upper member of the Fermi dyad.

The present selectivity in the shape resonance region can thus be rationalized in the same way as the selectivity in excitation of normal vibrations in polyatomic molecules, that is in terms of slope of the potential, determining the amount of momentum imparted to the nuclei during the short lifetime of the negative ion resonance [3]. Whereas the intensity in the usual case is given by the slope of the potential surface in the direction of the normal mode coordinate, the intensity of a Fermi-coupled vibration is given by the slope of the potential in the direction of the appropriate combination of the normal coordinates.

The selectivity in the threshold region can be understood in the same way under the plausible assumption that the virtual state has the effect of letting the nuclear wave function expand simultaneously in the directions of bending and symmetric stretch, similarly as the lower branch of the shape resonance.

The discussion may be closed with a few brief remarks: (i) In view of the selectivity observed in the present experiment at threshold it is remarkable that two vibrational

Feshbach resonances, with the two Fermi-coupled states as parents, have been observed with comparable intensity in the attachment of very low energy electrons to CO<sub>2</sub> clusters [23]. (ii) The excitation of the lower member of the Fermi dyad is seen to dominate at an incident electron energy of 5 eV (Fig. 2), in line with the observation made by Krenzer *et al.* [9] for CO<sub>2</sub> adsorbed on a silver surface. There is thus no need to postulate a different excitation mechanism for adsorbed CO<sub>2</sub>. (iii) An efficient excitation process for FR<sub>11</sub> is seen to be operative in the intermediate region 1–2.5 eV in Fig. 2. From the experimental point of view it acts as a broad <sup>2</sup>Σ<sub>g</sub> (σ\*) shape resonance connecting seamlessly to the virtual state at low energies. It overlaps with the <sup>2</sup>Π<sub>u</sub> shape resonance at high energy, indicating that vibrational excitation in this energy range is affected by vibronic coupling between resonances, as described for the general case by Estrada *et al.* [24]. (iv) The cross section for exciting the FR<sub>1</sub> state has a peculiar shape, a weaker structureless shoulder below 3.2 eV, and a structured band at higher energies. (v) Finally, vertically expanded spectra (not shown in Fig. 1 to improve clarity) indicate that higher lying combination vibrations affected by Fermi resonances, for example, the dyad resulting from mixing (11<sup>1</sup>0) and (03<sup>1</sup>0), are subject to selectivity similar to that discussed above: only the upper member is appreciably excited at threshold.

In conclusion, excitation of Fermi-coupled vibrations by electron impact is highly selective, the intensity borrowing known from Raman spectroscopy is not operative. The selectivity is interpreted as a consequence of the very short duration of the interaction of the incident electron with the target CO<sub>2</sub> which makes the excitation depend not only on which normal modes are contained in a given vibration arising from a Fermi resonance, but also on their relative phases. The present spectra further indicate that vibrational excitation in CO<sub>2</sub> below 5 eV is more complex than generally assumed, with a resonant mechanism in the intermediate energy range 1–2.5 eV and with vibronic coupling between this and the <sup>2</sup>Π<sub>u</sub> resonance.

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