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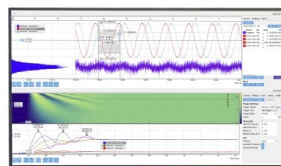
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A high resolution electron energy loss spectroscopy study of the Fermi resonance of CO₂ adsorbed on a Ag(110)/CO₃ layer

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The adsorption of CO₂ on a Ag(110) surface precovered with a saturated CO₃ layer has been studied by high resolution electron energy loss spectroscopy (HREELS). A weakly bound state of CO₂ is stabilized by the presence of carbonate. In addition to the losses of the bend (658 cm⁻¹) and the antisymmetric stretch (2343 cm⁻¹) fundamental modes, the presence of two peaks in the frequency region of the symmetric stretch mode have been observed. Such a loss pair is characteristic for the existence of a Fermi resonance, between the overtone of the bend and the symmetric stretch vibration, which had been studied in detail for the gas phase CO₂ molecule. By use of three CO₂ isotopomers the existence of the Fermi resonance in the adsorbed state has been verified and the Fermi constant and the energy of the unperturbed vibrations have been determined from the isotopic shifts. The character of the CO₂ molecule is almost unaffected by the bonding and it adsorbs in a tilted geometry. © 1999 American Institute of Physics. [S0021-9606(99)71527-8]

INTRODUCTION

The free CO₂ molecule presents the classical example of a general phenomenon in vibrational spectra, the Fermi resonance, which always occurs if two vibrational levels of different vibrations (or combinations) but belonging to the same symmetry species are energetically nearly degenerate. The point group of the linear CO₂ molecule is $D_{\infty h}$ and its vibrational spectrum should thus show three dipole active eigenmodes (two degenerate bending and the asymmetric stretch modes) and the Raman active symmetric stretch vibration. The Raman spectrum of CO₂ exhibited, however, two clear lines in the frequency region where only the symmetric stretch mode was expected.¹ The explanation of this result was given by Fermi² who realized that one of the overtones of the bending mode and the symmetric stretch mode of CO₂ are of the same symmetry species and almost degenerate, and thus the harmonic approximation breaks down. In effect the anharmonic terms in the force field of the molecule become important and the vibrational wave functions of the related modes are no longer decoupled. He treated this resonance in a perturbation approach by introducing an effective coupling, the Fermi constant, between the unperturbed wave functions. In consequence, the vibrational levels split into the so-called Fermi dyad and the corrected wave functions consist of a symmetric and antisymmetric combination of the unperturbed wave functions. This description accounts also for the observed line strength of the Fermi dyad since the overtone gains intensity from the fundamental. More detailed reviews are found in Refs. 3 and 4. Later studies of the CO₂ molecule used the isotope shifts of various isotopomers and the higher harmonics to determine not only the Fermi constant (and the unperturbed levels) but also the higher order anharmonic terms in the force field expansion.⁵⁻⁷

The adsorption state of the CO₂ molecule at single crystal metal surfaces has been studied for various systems. A chemisorption state has been identified for some reactive metals, like Fe or Co, with the CO₂ in a bent configuration due to the metal bond. On the majority of metals, however, CO₂ forms a very weak physisorption bond leaving the molecular orbitals essentially unchanged as can be deduced, for instance, from the vibrational spectrum almost identical to that of the free molecule (for an exhaustive survey see the review article by Freund⁸). The features observed in the frequency region of the Fermi resonance, however, are not interpreted in detail since most investigations have focussed on the more stable chemisorption state of CO₂ usually in connection with reactions. In coadsorption systems weakly adsorbed CO₂ has been noticed quite often as a side product in reaction studies, but the two losses observed have been attributed to the Fermi dyad without further elaboration (see Refs. 9-13 for a selection). On clean surfaces, physisorbed CO₂ usually exhibits only one dominant peak which has been assigned to either the overtone of the bending mode or the symmetric stretch, also without a detailed discussion.^{11,12} On the Ag(111) surface the CO₂ physisorption state has been studied at 40 K up to the multilayer regime with HREELS but the resolution was too low to resolve the Fermi dyad. Only through variation of the primary energy the existence of the Fermi resonance could be deduced since the peak center of the corresponding peak shifts due to the energy dependence of only the symmetric stretch loss intensity.¹³

In the course of our HREELS investigations into the formation of CO₃ on Ag(110) by reacting CO₂ with preadsorbed oxygen,¹⁴ we noticed that on a well ordered saturated CO₃ layer adsorption of CO₂ becomes stabilized up to 130 K. This has been observed previously¹⁰ but not further investigated. Since adsorption and desorption of CO₂ does not essentially affect the carbonate layer it is possible to prepare CO₂ in a very weakly bonding adsorption state which clearly

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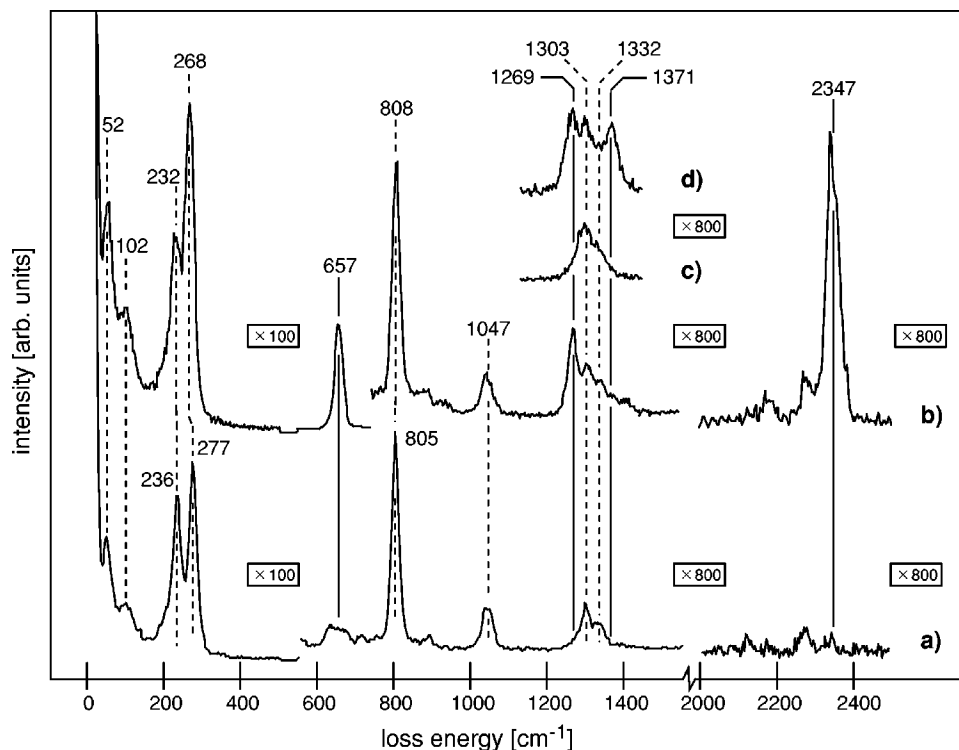


FIG. 1. HREEL spectra of (a) saturated $^{13}\text{C}^{16}\text{O}_3$ layer, (b) after exposure to 1000 mbar s of $^{12}\text{C}^{16}\text{O}_2$ measured at 5 eV primary energy. Spectra (c) and (d) present the same sequence in the region of the Fermi resonance but measured with 10 eV primary energy. The dashed lines indicate the CO₃ related peak, and solid lines the structures of the adsorbed CO₂.

shows the Fermi dyad in the vibrational spectrum. In order to assign the losses in the resonance region and to extract the Fermi constant and the position of the unperturbed modes we performed a systematic study of the vibrational spectrum of CO₂ employing the $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$, and $^{12}\text{C}^{18}\text{O}_2$ isotopomers.

EXPERIMENT

The usual recipe of extensive argon ion sputtering and subsequent annealing to 650 K was used to obtain a clean Ag(110) substrate which was checked with LEED and by the ease of producing the full ($n \times 1$) sequence of the oxygen induced reconstructions.¹⁵ The EEL spectrometer is a double pass instrument (HIB 1000, VSW, Ibach design¹⁶) operated at a primary energy of either 5 or 10 eV with an incidence angle of 60°. The scattering plane was coincident with the [110] azimuth. Some off-specular spectra were collected at $\Delta\theta \sim 5^\circ$ by setting the incidence angle to 65° while retaining the detection angle at 60°. Typically, the resolution was in the range 16–24 cm⁻¹ with a slight degradation off-specular. Both O₂ and CO₂ were exposed via a capillary doser system. Commercially available CO₂ isotopes were used with a purity of 99%; only the $^{12}\text{C}^{18}\text{O}_2$ contained ~1% of $^{12}\text{C}^{16}\text{O}_2$ admixtures as was verified with the mass spectrometer. The preparation of the carbonate preadsorption layer is described in full detail in Refs. 14 and 17. It showed a sharp (1×2) LEED pattern with intense overlayer reflexes and did not contain atomic oxygen remaining from the formation reaction.

RESULTS AND DISCUSSION

The vibrational spectrum of the stabilizing preadsorption layer of carbonate on the Ag(110) surface is displayed in Fig. 1(a). From the various isotopomers of CO₃ studied in the foregoing investigation¹⁷ the $^{13}\text{C}^{16}\text{O}_3$ species was chosen as it has the least positional overlap in the frequency region of the Fermi resonance of CO₂. The carbonate layer was prepared by reacting a saturated molecular oxygen layer with CO₂ followed by a flash to 400 K thus providing a well-ordered layer of pure carbonate without residual oxygen thereas excluding any further reaction with CO₂. The intense losses around 260 cm⁻¹ are due to CO₃-substrate vibrations. The peaks at 805 and 1047 cm⁻¹ are assigned to the out-of-plane bending and the symmetric stretch modes, respectively. The asymmetric stretching vibration, which is degenerate in solution, occurs at ~1300 cm⁻¹ and is slightly split. The other degenerate mode, the in-plane bend, is not detectable at the primary energy of 5 eV used in Fig. 1(a) but is clearly present at 10 eV located at 712 cm⁻¹. A detailed discussion of the formation and vibrational modes of CO₃ will be published presently.¹⁷ The spectrum obtained upon adsorbing ~1000 mbar s $^{12}\text{C}^{16}\text{O}_2$ is shown in Fig. 1(b). The additional loss structures are due to adsorbed CO₂ and can be removed by heating the substrate above 130 K, the temperature at which the desorption maximum occurred in the thermal desorption spectrum. The positions of the CO₃ losses remain almost unaffected, only the frustrated modes are distinctly shifted to lower frequency and the intensity of the structure at 236 cm⁻¹ is suppressed. This effect strongly suggests the CO₂ to be locally bonded at the CO₃ anion. It

TABLE I. Observed and calculated frequencies of different CO₂ isotopomers.^a

	¹² C ¹⁶ O ₂			¹³ C ¹⁶ O ₂			¹² C ¹⁸ O ₂		
	Gas phase ^b	This work	Calculated	Gas phase ^b	This work	Calculated	Gas phase ^b	This work	Calculated
δ	667	657		649	638	638	657	649	647
ν^-	1285	1262		1265	1240		1230	1226	
ν^+	1388	1372		1370	1354		1347	1322	
$\delta^{(2)}$	1340 ^c		1316	1302 ^c		1276			1294
ν_s	1334 ^c		1318	1334 ^c		1318			1250
ν_{as}	2349	2347		2284	2277	2280	2314	2309	2311
W	52.84 ^c		55	51.34 ^c		53	50.52 ^c		42

^aAll values in cm⁻¹.^bGas-phase values from Rothman (Ref. 18).^cThese calculated values are taken from Suzuki (Ref. 6).

was possible to desorb and readsorb CO₂ several times without any changes in the CO₃ spectrum, thus indicating that the carbonate layer functions merely as a support.

The CO₂ induced losses at 657 and 2347 cm⁻¹ are easily assigned to the degenerate bend (δ) and the asymmetric stretch (ν_{as}) modes. A comparison with the gas phase values is given in Table I and shows that the adsorption induces an overall red shift of only a few wave numbers. The same applies to the isotopically substituted CO₂ molecules which were measured and these are also compared to gas phase values shown in Table I. A difficulty arose with the ¹²C¹⁸O₂ where some admixture with ¹²C¹⁶O₂, the main impurity in the dosing gas, was always observed on the surface and was overrepresented in the ν_{as} peak via intensity borrowing. It was, however, possible to remove this contribution by subtraction and reliably determine the correct frequency. In addition, Table I shows the isotopic shifts calculated with respect to ¹²C¹⁶O₂ by inserting the corresponding masses into the equations of the eigenfrequencies given in Herzbergs book.⁴ These equations are based on the solution of the secular equation in harmonic approximation and work quite well for the relative values of isotopic shifts. However, to generate the whole spectrum with its overtones, a more complete analysis with higher order terms in the potential approximation would have to be done—the absolute frequencies calculated from experimentally determined force constants deviate, in part significantly, from the measured data. The calculated numbers agree almost perfectly with the observed values and indicate that the CO₂ molecule maintains its linear geometry upon adsorption. The presence of both the δ and the ν_{as} modes in the spectrum is only compatible with a tilted configuration since the former is polarized perpendicular to the molecular axis, the latter parallel. This result is in full accordance with the general trend observed in several studies of the weakly bound form of CO₂ (see Ref. 8, and references therein).

In the frequency region, where for the free molecule the Fermi resonance is observed, CO₂ adsorption gives rise to a pronounced peak at 1269 cm⁻¹, while only a small intensity increase is observed above the doublet feature of CO₃. In their HREELS investigation of physisorbed CO₂, Sakurai *et al.*¹³ have observed that the loss intensity of the features in this region passes a maximum at about $E_p \sim 10$ eV, although

they were unable to resolve the Fermi dyad. The spectrum of the relevant region measured at a primary energy of $E_p = 10$ eV is shown in Figs. 1(c) and 1(d), before and after adsorption of CO₂. At that energy the higher loss of the Fermi dyad becomes evident at 1371 cm⁻¹. The enhancement is connected with an intramolecular resonance as it is also observed for the free molecule,¹⁹ and affects predominantly the symmetric stretch vibration. The fundamental of the δ mode shows no comparable feature. Making use of this property we measured three CO₂ isotopomers at $E_p = 10$ eV. The results in the relevant region are shown in Fig. 2 as difference spectra with the carbonate contributions being subtracted to emphasize the CO₂ induced losses. Prior to

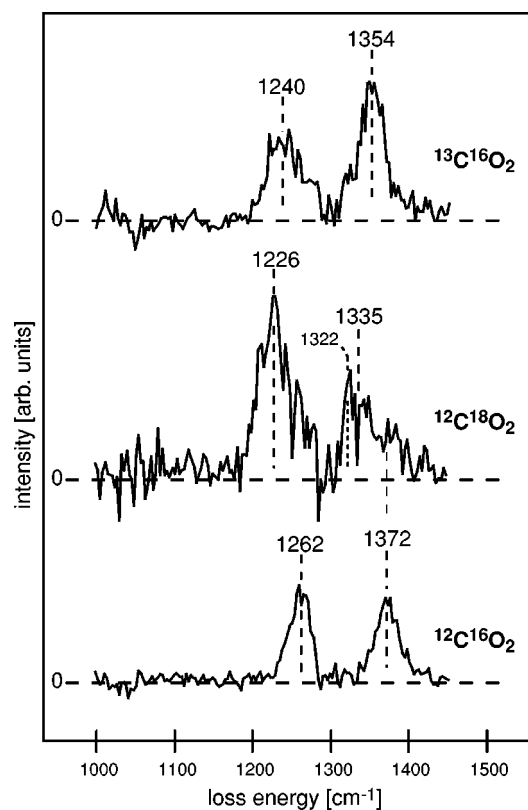


FIG. 2. Difference spectra of three CO₂ isotopomers indicated at the curves with the pure ¹³C¹⁶O₃ layer. Primary energy 10 eV.

subtraction the related spectra were normalized at 1300 cm⁻¹, a procedure which was found to be the most reliable with respect to avoid artifacts. It should be noted that, as discussed above in connection with the asymmetric stretch vibration, the ¹²C¹⁸O₂ spectrum shows contributions from ¹²C¹⁶O₂ impurities from the dosing gas, which leads to an apparent upward shift of the raw peak in Fig. 2. By subtracting the respective contributions the true frequency has been determined. The frequencies of the Fermi dyads of the isotopomers are listed in Table I as ν^- and ν^+ .

An inspection of the numbers in Table I immediately reveals that it is not possible to assign the two losses ν^- and ν^+ to the overtone $\delta^{(2)}$ of the bending and the fundamental of the symmetric stretch modes, respectively. The latter must show the same frequency between the ¹²C¹⁶O₂ and the ¹³C¹⁶O₂ isotopes from symmetry considerations while the experiment yields a distinct shift. Similarly, the ν^- peak of the ¹²C¹⁸O₂ exhibits a lower frequency than that of ¹³C¹⁶O₂ although the δ mode fundamentals show the inverse order. It is evident that ν^- and ν^+ belong to a Fermi dyad and must be analyzed accordingly. Following Herzberg,⁴ first order perturbation theory yields for the shifted frequencies,

$$\nu^\pm = \bar{\nu} \pm \frac{1}{2} \sqrt{4W^2 + \Delta^2}, \quad (1)$$

$$\bar{\nu} = \frac{1}{2}(\delta^{(2)} + \nu_s) \quad \text{and} \quad \Delta = \delta^{(2)} - \nu_s, \quad (2)$$

with W the Fermi constant. It follows from Eq. (1) that the arithmetic mean of the respective loss pairs is conserved between the perturbed and unperturbed energies. This can be used to calculate the unperturbed levels from the experimental data of the three isotopomers independently from W assuming an anharmonic shift in the simplest approximation²⁰

$$\delta^{(2)} = 2\delta(1 - 2x_e), \quad (3)$$

with x_e the anharmonicity coefficient being the same for all isotopomers. As an additional input we use

$$\nu_s(^{12}\text{C}^{16}\text{O}_2) = \nu_s(^{13}\text{C}^{16}\text{O}_2) = \sqrt{\frac{18}{16}} \times \nu_s(^{12}\text{C}^{18}\text{O}_2). \quad (4)$$

The last equation gives the relative isotopic shift from the formula given in Ref. 4. As there are two unknowns, ν_s and x_e , and three equations, we were able to check the internal consistency of the interpretation. The anharmonicity parameter was found to be in the order of 10⁻³ which agrees quite well with the gas phase results,^{6,7} but is here negligible in view of our experimental resolution. The isotopic shift of $\nu_s(^{12}\text{C}^{18}\text{O}_2)$ yielded 0.9484 × $\nu_s(^{12}\text{C}^{16}\text{O}_2)$ as compared to 0.9428 calculated from Eq. (4), in almost exact agreement. The calculated values are also listed in Table I. A schematic level diagram of the vibrational energies is displayed in Fig. 3 showing the calculated (unperturbed) in comparison with the observed levels. The energetic degeneration of the unperturbed frequencies for the ¹²C¹⁶O₂ isotope is nearly perfect and the Fermi resonance shift corresponds directly to the strength of the coupling [see Eq. (1)]. The symmetric stretch frequency is slightly above the overtone in contrast to the gas phase analysis where the frequency of the fundamental is

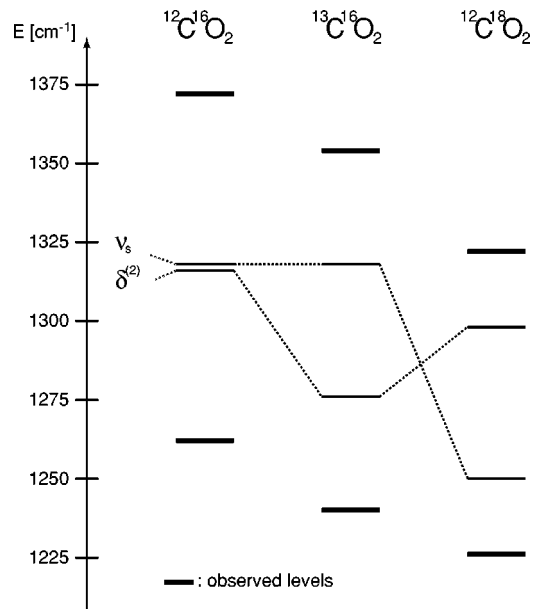


FIG. 3. Energy level diagram of the Fermi dyad and the calculated unperturbed vibration niveaus of the $\delta^{(2)}$ overtone and the ν_s fundamental modes for three isotopomers of CO₂.

lower than that of the overtone (see Table I and Refs. 5 and 6). It should be noted, however, that the position of the energy levels of the symmetric stretch and the overtone, and thus the assignment to the two modes, is dependent on the density of the CO₂, as a study by Garrabos *et al.* has shown.²¹ In the case of ¹³C¹⁶O₂ the states are initially separated by ~40 cm⁻¹ with the same ordering of the uncoupled states. Both cases result in a Fermi constant of ~50 cm⁻¹ which is almost the same number as derived from the gas phase data. For the ¹²C¹⁸O₂ the ordering is reversed, the fundamental is below the overtone. The Fermi constant determined for this isotope is significantly smaller, ~40 cm⁻¹, in contrast to the free molecule. The reason for this deviation is not clear. In general, the agreement of the values determined in this work for the adsorbed CO₂ proves that the internal electronic structure is almost unchanged upon adsorption at the Ag(110)/CO₃ surface.

The intensity ratio of the Fermi dyad shown in Fig. 2 reflects to a high degree the behavior expected from the theory. In first order perturbation theory the perturbed wave functions are given by a symmetric and an antisymmetric linear combination of the unperturbed functions, with coefficients determined by the interaction and the initial energy distance (see Ref. 4). The intensity of the detected losses in the Fermi resonance case is proportional to the coefficient of the fundamental, i.e., its contribution to the combinations, since only the fundamental, here the symmetric stretch, is excited with a normal intensity while an overtone has typically an excitation probability of only some percent of its fundamental.²⁰ For fully degenerate levels the coefficients are equal and thus the loss pair should have equal intensity. This is seen in the spectrum of ¹²C¹⁶O₂ in Fig. 2. If the unperturbed levels are split, the order of the levels is unchanged as they only repel each other; the coefficients are different and the wave function of the perturbed upper level

has always the stronger admixture of the unperturbed one, and vice versa. This is clearly reflected in Fig. 2. For both the $^{13}\text{C}^{16}\text{O}_2$ and the $^{12}\text{C}^{18}\text{O}_2$ isotopomer, the ν_s derived peak is more intense. It must be noted, however, that the agreement of the intensities only applies for a primary energy of 10 eV, where the resonant enhancement of the symmetric stretch occurs. At 5 eV, it is always the lower frequency peak which is dominant in the CO_2 spectra for all isotopomers measured. This effect is already visible in Fig. 1(b) where the loss at 1371 cm^{-1} contributes a clear but very weak signal. The frequency is identical for both primary energies proving that the Fermi resonance behavior is detected. The reason for the apparent incompatibility with the theoretical description is yet unresolved. This phenomenon may also explain why in the majority of previous studies of weakly coadsorbed CO_2 (Refs. 10–12) the only dominating peak has been detected in the Fermi resonance region.

SUMMARY

The vibrational signature of CO_2 stabilized at 100 K on a Ag(110) surface precovered with carbonate has been studied by HREELS. In addition to the bending and the antisymmetric stretch mode fundamentals observed at almost the energies of the free molecule, the Fermi dyad in the frequency region of the symmetric stretch vibration was detected. By tuning into the molecular resonance for the symmetric stretch mode at 10 eV the loss pair could be easily separated from the carbonate contributions in the spectra. From the measurement of all frequencies for three CO_2 isotopomers ($^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{18}\text{O}_2$) we have uniquely verified the existence of the Fermi resonance in the adsorbed CO_2

molecule and extracted from the measured frequencies, both the positions of the unperturbed vibrational energies and the Fermi constant for the three isotopomers. Apart from a slight red shift the vibrational properties demonstrate that the molecule retains its linear geometry with the molecular axis tilted with respect to the surface normal.

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