reasonably well with a weak feature found in the electron-energy-loss spectrum at 5.85 eV.<sup>7</sup> A feature in the experimental spectrum at 6.04 eV has been previously assigned as the  $2^{1}B_{\mu}$ state.7 Given the error in our calculated ionization potential, it is unrealistic to attempt to choose between these two features based on the calculated results.

One question which remains unanswered by the present study is the cause of the seeming disappearance of the  $2^{1}A_{e}$  state in the gas-phase fluorescence spectrum. Our results indicate that in relaxed excited-state geometries the  $2^{1}A_{g}$  state is found to lie significantly below the  $1^{1}B_{u}$  state. Since the calculations are performed on the isolated molecule, the cause of this discrepancy remains unresolved. Clearly further work is required to answer this question.

#### V. Conclusion

Results are presented from ab initio CI calculations for several low-lying excited states of all-trans-octatetraene. In a vertical transition from the ground state the lowest singlet excited state is found to be of  ${}^{1}B_{\mu}$  symmetry. This state is essentially valencelike.

The second excited singlet state is a  $2^{1}A_{g}$  state at the ground-state geometry, the zeroth-order description of which is multiconfigurational and can be identified with the so-called "doubly excited" state found in long-chain polyenes. However, application of a correction for the 2<sup>1</sup>A<sub>g</sub> state based on the estimated 0-0 transition energy makes the  $1^{1}B_{u}$  and  $2^{1}A_{g}$  states essentially degenerate at the ground-state geometry. Relaxation of the excited-state geometries leads to the  $2^{1}A_{g}$  state having the lowest 0–0 transition energy. Reasonable agreement is found with experiment where comparisons can be made, and we predict that the  $2^{1}B_{\mu}$  state is of 3p<sub>x</sub> Rydberg character and lies near 5.65 eV.

Acknowledgment. We gratefully acknowledge financial support of this research by the National Insitute of Health, Grant 2 R01 GM34081-03. The calculations were performed at the Indiana University Chemistry Computational Facility, the establishment of which was in part made possible by grants from the National Science Foundation, Grants CHE-83-09446 and CHE-84-05851.

Registry No. all-trans-Octatetraene, 3725-31-3.

# Fourier Transform Infrared Studies of Atomic Ti, V, Cr, Fe, Co, Ni, and Cu Reactions with Carbon Dioxide in Low-Temperature Matrices

# J. Mascetti\* and M. Tranquille

Laboratoire de Spectroscopie Moléculaire et Cristalline, UA 124 CNRS, Université de Bordeaux I, 351, Cours de la Libération, 33405 Talence Cedex, France (Received: February 11, 1987; In Final Form: October 20, 1987)

Titanium, vanadium, chromium, iron, cobalt, nickel, and copper metal atoms were cocondensed with CO<sub>2</sub> in neat matrices at 15 K. Even though a large proportion of atoms do not react, new complexes with CO<sub>2</sub> are characterized by using FTIR techniques and their infrared absorption bands are assigned. It is clearly shown that  $CO_2$  is highly bent in these complexes. The behavior of oxophile metals is different from that of other metals which spontaneously form 1:1 complexes with CO2. For Ti, V, and Cr, we observe first an insertion of metallic atom into a CO bond, leading to the formation of the intermediate (O)M(CO) molecule, followed by the CO<sub>2</sub> fixation on this complex, to form  $(O)M(CO)(CO_2)$ . The other identified products in the matrices are CO, M(O),  $M(CO)_m$  and possibly a few carbonates. Most complexes are thermally unstable and decompose above 60 K. Only Fe and Ni compounds give rise upon annealing above 80 K to  $CO_2$  reduction to CO along with the simultaneous formation of metal carbonyl complexes. Isotopic experiments with <sup>13</sup>CO<sub>2</sub> and C<sup>18</sup>O<sub>2</sub> allow us to conclude that the geometry of complexes is both metal and matrix dependent: in neat CO2 matrices, Fe and Co lead to a "C coordination", the others being fixed in a "side-on" or "end-on" manner.

#### I. Introduction

During the past 12 years there has been a considerable growth of interest in the reactions of  $CO_2$  because of the need to develop alternative hydrocarbon sources.<sup>1-4</sup>  $CO_2$  is potentially the most abundant source of  $C_1$  chemistry but new ways must be found to activate the molecule catalytically if its potential has to be realized. Activation is one of the routes to induce inert molecules to react. Some transition-metal atoms in the low valency state form complexes with  $CO_2$ . Such complexes have potential for practical application in activating  $CO_2$ .  $CO_2$  displays several modes of coordination with metallic compounds. Bonding between  $CO_2$  and metals may lead to the following intermediate compounds:5



Structures of type A were proposed from ab initio calculations<sup>6</sup> and from IR results reported by Kafafi and co-workers<sup>7</sup> for the  $LiCO_2$  complex of  $C_s$  symmetry. Type D structures were only encountered when M is an alkali-metal atom and observed by RPE

<sup>(1)</sup> Volpin, M. E.; Kolomnikov, I. S. Organometallic Reactions; Wiley-Interscience: New York, 1970; Vol. 5, p 313.

<sup>(2)</sup> Sneeden, R. P. A. Actual. Chim. 1979, 1, 31; 1979, 2, 22.
(3) Lapidus, A. L.; Ping, Y. Y. Russ. Chem. Rev. 1981, 50, 63.
(4) Ziessel, R. Nouv. J. Chim. 1983, 7, 613.
(5) Stankevich, I. V.; Lysyak, T. V.; Aleksandrov, G. G.; Kolomnikov, I. S. J. Struct. Chem. 1978, 19, 777.

<sup>(6)</sup> Sakaki, S.; Kitaura, K.; Morokuma, K. Inorg. Chem. 1982, 21, 760. (7) Kafafi, Z. H.; Hauge, R. H.; Billups, W. E.; Margrave, J. L. J. Am. Chem. Soc. 1983, 105, 3886.

TABLE I: IR Ranges of Wavenumbers for Various Metallic CO2 Compounds<sup>a</sup>

CO <sub>2</sub> compounds	IR wavenumbers, cm <sup>-1</sup>
CO <sub>2</sub> Co	mplexes
side- on M (1-5)	1780–1620, 1300–1100, 900–800, 600–400
71-C M-C	1650-1550, 1280-1180
η <sup>1</sup> -0 M-0=== C <sup>-0</sup> (7)	1751, 1221, 739, 611 (M = Li)
Carbonate Co	omplexes (30)
unidentate M-0-C	1500–1450, 1380–1360, 1070
bidentate M	1640–1590, 1290–1260, 1030
tridentate M	1480-1460, 1360-1350, 820, 500
Oxalate Cor	nplexes (30)
head-to-tail M	1760–1720, 1680–1600, 1510, 1340–1290, 1000, 790
head-to-head M	1700–1650, 1400–1250, 900, 800, ν < 500
Formate and Carbox	ylate Complexes (30)
M-0-c	1590–1540, 1370–1330
мс-н. р	1420, 800, 690

Metal-Carboxylic Acids and Metal Carboxylates (30) 1640-1545, 1430-1395, 620 О—н. в

<sup>a</sup> Values were obtained from the references indicated in parentheses.

TABLE II: UV-Visible Maxima (nm) Observed in M/CO<sub>2</sub> (1/1000) Deposits, in Addition to Absorptions Due to Unreacted Atoms

$Ti/CO_2$	341, 352, 389, 442
$Ni/CO_2$	244, 254, 338, 347, 399
$Cu/CO_2$	229, 249, 263, 323, 342, 409, 549

or IR spectroscopies for LiCO2,78 NaCO2,9 KCO2,910 and CsCO2,9

Structures of types B and C are those generally encountered with transition-metal atoms and some examples are described in the literature. As far as we know, only six structures have been determined by diffraction methods:

type B:

 $[(\text{pr-salen})\text{Co}(\text{CO}_2)]^-\text{K}^+$  (ref 11)

$$(PMe_3)_3Ir(C_2O_4)Cl$$
 (ref 12)

(8) Borel, J. P.; Faes, F.; Pittet, A. J. Chem. Phys. 1981, 74, 2120.
(9) Jacox, M. E.; Mulligan, D. E. Chem. Phys. Lett. 1974, 28, 163

- (10) Bennet, J. E.; Mile, B.; Thomas, A. J. Chem. Soc., Faraday Trans. 1 1965, 61, 2357.
- (11) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. J. Am. Chem. Soc. 1982, 104, 5082
- (12) Merskovitz, T.; Guggenberger, L. J. J. Am. Chem. Soc. 1976, 98, 1615.
- (13) Dohring, A.; Joly, P. W.; Kruger, C.; Romao, M. J. Z. Naturforsch. 1985, 40b, 484.
- (14) Bristow, G. S.; Hitchcock, P. B.; Lappert, D. M. J. Chem. Soc., Chem. Commun. 1981, 1145.
- (15) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. J. Am. Chem. Soc. 1985, 107, 2985.
- (16) Alvarez, R.; Carmona, E.; Guttierez-Puebla, E.; Marin, J. M.; Monge, A.; Poveda, M. J. Chem. Soc., Chem. Commun. 1984, 1326.
- (17) Huber, H.; McInstosh, D.; Ozin, G. A. Inorg. Chem. 1977, 16, 975; 1978. 17. 1472
- (18) Kurtikian, T. S.; Kazarian, S. G. Arm. Khim. Zh. 1981, 34, 375.



Figure 1. UV and visible spectra of Ti (a), Ni (b), and Cu (c) atoms cocondensed with pure CO<sub>2</sub> at 15 K (M/CO<sub>2</sub> ~ 1/1000) (hatching represents absorption bands of  $MCO_2$  complexes).



Figure 2. IR spectrum of a solid thick CO<sub>2</sub> sample at 15 K.

type C:  $(PCy_3)_2Ni(CO_2)$  (ref 13)  $(\eta^5 - C_5 H_4 Me)_2 (CH_2 Si Me_3) Nb(CO_2)$  (ref 14)  $Cp_2Mo(CO_2)$  (ref 15)  $(i-Pr-NC)(PMe_3)_3Mo(CO_2)_2$  (ref 16)

Table I lists all the observed bands in the infrared region for various CO2 metallic compounds. Nevertheless, few spectroscopic studies have been performed on CO<sub>2</sub> complexes with zerovalent metals; the formation of  $\pi$ -complexes Au(CO<sub>2</sub>), Ag(CO<sub>2</sub>),<sup>17</sup> and  $Cu(CO_2)^{18}$  have been claimed but their infrared spectra have not been published yet.

So, it appears to us that a convenient route to the preparation of transition-metal- $CO_2$  complexes and their identification by means of vibrational spectroscopy might be obtained through the cocondensation reaction of metal atoms with CO2 at cryogenic temperatures.<sup>19,20</sup> This FTIR study has been undertaken in an attempt to learn more about the binding of CO<sub>2</sub> with transition-metal atoms and the new species formed. Some preliminary results have already been published<sup>21</sup> and we report here the final conclusions of several matrix isolation experiments in which metal atoms were cocondensed with pure or diluted CO<sub>2</sub> at 15 K. After a brief description of the experimental procedure in section II, we shall present in section III the results obtained by UV-visible and infrared spectroscopies, showing the essential role played by the FTIR technique in such studies. In section IV, we propose some reactivity pathways for the different transition metals. In section V, we present the results of a normal-coordinate analysis leading to the approximate force constants of bonded  $CO_2$ .

- (21) Mascetti, J.; Tranquille, M. Surf. Sci. 1985, 156, 201.

<sup>(19)</sup> Moskovits, M.; Ozin, G. A. Cryochemistry; Wiley-Interscience: Toronto, Canada, 1976. (20) Tranquille, M. Images Chim. 1980, 36, 18



Figure 3. IR spectra of the cocondensation reaction products of transition-metal atoms with pure  $CO_2$  at 15 K (M/ $CO_2 \sim 1/1000$ ). (Bands arising from H<sub>2</sub>O at 1615 cm<sup>-1</sup> and CO<sub>2</sub> have been omitted for clarity.)

TABLE III: Frequencies and Tentative Assignments of the Main Infrared Bands Observed in  $M/CO_2$  (1/1000) Deposits at 15 K, in Addition to H<sub>2</sub>O Absorption (1615 cm<sup>-1</sup>) and Unreacted CO<sub>2</sub>

	frequencies, cm <sup>-1</sup>						tentative
Ti	V	Cr	Fe	Co	Ni	Cu	assignt
1735	1745	1692	1565 1210	1625 1190	1818	1716	$\nu(C=0) \\ \nu_a(COO) \\ \nu_s(COO)$
1132	1176	1095			1131 744	1215 718	ν(C–O) δ(OCO)

# **II. Experimental Section**

Atoms were generated by directly heating a thin ribbon (20  $\times$  5  $\times$  0.5 mm) of the appropriate metal, strung between water-cooled copper electrodes except for Cu which was wrapped around a niobium filament and for Cr which was evaporated from crystals in a small tungsten basket. Metals were supplied by Goodfellow Metals (Ti 99.6%, V 99.8%, Fe 99.99%, Co 99.9%, Ni 99.98%, Nb 99.9%) and by Prolabo (Cr and Cu 99.9%). CO<sub>2</sub> (99.995%) and Ar (99.995%) were supplied by Air-Liquide and used without further purification.

The furnace for metal vaporizations and the complete apparatus have been described previously.<sup>22</sup> In addition to <sup>12</sup>C<sup>16</sup>O<sub>2</sub>, isotopically substituted carbon dioxide <sup>13</sup>C<sup>16</sup>O<sub>2</sub> (enriched up to 90%) and <sup>12</sup>C<sup>18</sup>O<sub>2</sub> (enriched up to 97%), provided by the Commissariat à l'Energie Atomique, were used to identify reaction products and assign vibrational bands.

The matrix ratios used were M/gas  $\simeq 1/1000$  in moles per mole. The metal deposition rate was continuously controlled by using a quartz crystal microbalance. The metal, CO<sub>2</sub>, and eventually argon gases (CO<sub>2</sub>/Ar = 1/10) were cocondensed over 4 h (infrared experiments) or 1 h (UV-visible deposits).

For infrared studies, matrices were deposited on a CsI window cooled at 15 K by means of a Cryophysics closed cycle refrigerator, Cryodine 21. Infrared spectra were recorded with a Bruker 113 V interferometer. Band wavenumbers were measured with an accuracy of  $\pm 2 \text{ cm}^{-1}$ . In UV-visible experiments, matrices were deposited on a NaCl window and spectra in the range 210–700 nm were recorded on a Perkin-Elmer E1 spectrometer, interfaced to a data station Minc-Digital.

The Journal of Physical Chemistry, Vol. 92, No. 8, 1988 2179



Figure 4. IR spectra  $\gamma$  reaction products of titanium atoms with pure CO<sub>2</sub> after deposition at 15 K (a) and after annealing up to 53 K (b), with mixed CO<sub>2</sub>/O<sub>2</sub> (3/1) matrix (c), with neat O<sub>2</sub> matrix (d).

#### **III. Results**

1. UV-Visible Spectra of  $CO_2$  Deposits with Metal Atoms. UV-visible spectra were recorded for Ti/CO<sub>2</sub>, Ni/CO<sub>2</sub>, and Cu/CO<sub>2</sub> systems, always using a low molar ratio, M/CO<sub>2</sub> ~ 1/1000. These spectra are shown in Figure 1 and exhibit, besides atomic absorption bands, a few weak bands assigned to new compounds formed in the matrix. Table II lists the wavelength maxima observed for these systems. We thus propose the following conclusions: (a) with the concentrations used in our experiments, only metallic atoms are isolated in the matrix with no aggregate detected; (b) a small fraction of metallic atoms react with CO<sub>2</sub>, even within neat matrices; (c) the copper complex exhibits a set of bands similar to those observed by Ozin for Ag and Au complexes.<sup>17</sup>

2. IR Spectra of  $CO_2$  Deposits with Metal Atoms. With use of FTIR techniques, it is now possible to observe IR bands due to coordinated  $CO_2$  in addition to the intense bands due to unreacted  $CO_2$ . After a brief description of the IR spectrum of solid  $CO_2$ , we present several IR spectra of  $CO_2$  coordinated with first-row transition-metal atoms.

2.1. IR Spectrum of  $CO_2$  at Low Temperature. Gaseous  $CO_2$  is a linear  $D_{\infty h}$  triatomic molecule with three fundamental modes of vibration:

$$\begin{array}{c} - 0 = 0 = 0 \\ \nu_1 \\ (1285, 1388 \text{ cm}^{-1}) \\ (687 \text{ cm}^{-1}) \end{array} \xrightarrow{\nu_2} (2349 \text{ cm}^{-1}) \\ \end{array}$$

By convention,  $\nu_1$  and  $\nu_3$  are referred to as the symmetric and asymmetric stretching modes whereas  $\nu_2$  is the degenerate bending mode. The centrosymmetrical nature of free CO<sub>2</sub> molecule leads to mutual exclusion restrictions on the vibrational activities, and as a result,  $\nu_1$  is Raman active while  $\nu_2$  and  $\nu_3$  are IR active. Apart from weak bands due to natural <sup>13</sup>CO<sub>2</sub> abundance and overtones or combination bands, the presence of a Fermi resonance between  $\nu_1$  and  $\nu_2$  at 1285/1388 cm<sup>-1</sup> in the Raman spectrum must be borne in mind.

The IR spectrum of a thick sample of solid CO<sub>2</sub> cooled at 15 K on a CsI plate is presented in Figure 2. In addition to the two major bands ( $\nu_2$  and  $\nu_3$ ) several weaker bands are also observed at 2042 (m), 1934 (vw), 1914 (vw), 1615 (m), 1384 (m), 1277 (w) cm<sup>-1</sup>, and in the 700-800-cm<sup>-1</sup> region (weak broad bands). The bands at 1384 ( $\nu_1$ ) and 1277 cm<sup>-1</sup> ( $2\nu_2$ ) become IR active in the solid state. Absorption at 1615 cm<sup>-1</sup> is due to monomeric H<sub>2</sub>O units in the deposit. Bands at 2042, 1934, and 1914 cm<sup>-1</sup> are assigned to combination bands. These results are consistent with the previously reported low-temperature IR spectrum of CO<sub>2</sub>.<sup>23</sup>

<sup>(22)</sup> Cossé-Mertens, C. Thèse 3e cycle, Université de Bordeaux I, 1980.

TABLE IV: IR Band Frequencies Observed for Ti/CO<sub>2</sub>, Ti/<sup>13</sup>CO<sub>2</sub>, and Ti/C<sup>18</sup>O<sub>2</sub> Deposits (Ti/CO<sub>2</sub> ~ 1/1000) at 15 K

	IR freq, $cm^{-i}$ ( $\Delta \bar{\nu}$ , $cm^{-i}$ )			
<sup>12</sup> C <sup>16</sup> O <sub>2</sub>	<sup>13</sup> C <sup>16</sup> O <sub>2</sub>	<sup>12</sup> C <sup>18</sup> O <sub>2</sub>	assignments	
 2138	2089 (51)	2085 (55)	$\nu(CO)$ (carbon monoxide)	
2100	2065 (35)	2060 (40)	$u(\mathbf{CO})$ (titanium carbonyle)	
1946	1915 (31)	1905 (41)	V(CO) (Intallium carbonyis)	
1776, 1735	1730, 1702 (46, 33)	1740, 1710 (36, 25)	$\nu(C==O)$	
1615	1615 (0)	1615 (0)	$\delta(H_2O)$	
1132	1120 (12)	1100 (32)	$\nu(C-O)$	
988, 955	988, 955 (0, 0)	950, 920 (38, 35))		
895	895 (0)	860 (35)	$\nu(Ti=0)$	
885	885 (0)	845 (40)		



Figure 5. IR spectra of reaction products of titanium atoms with a mixed  $CO_2/^{13}CO_2$  (1/1) matrix (a) and with a mixed  $CO_2/C^{18}O_2$  (1/1) matrix (b) at 15 K.

2.2. IR Spectra of Coordinated  $CO_2$  at Low Temperature. A point of great interest concerning the vibrational properties of  $CO_2$ relates to its bonding in transition-metal complexes. As shown in Table I for known transition-metal  $CO_2$  compounds, characteristic IR absorptions occur in the 1750–1550- and 1350– 1150-cm<sup>-1</sup> regions. The position and number of absorption bands which can be assigned to vibrations of  $CO_2$  in these complexes indicate a marked decrease in both the CO bond order and the symmetry of the triatomic ligand upon complexation.

Several experiments have been performed with Ti, V, Cr, Fe, Co, Ni, and Cu in pure CO<sub>2</sub> using low metal concentration  $(M/CO_2 \sim 1/1000 \text{ molar ratio})$  in order to avoid aggregation. All condensations gave rise to colorless matrices, except for Cu/CO<sub>2</sub> deposits which were pink.

The resulting infrared spectra are presented in Figure 3. For clarity, bands arising from  $CO_2$  and  $H_2O$  (1615 cm<sup>-1</sup>) have been omitted. Most frequencies and tentative assignments are listed in Table III. In all these spectra, several new absorptions are detected which can be assigned to  $CO_2$ -metal complexes, according to literature data (compare Tables I and III). It is noteworthy that FTIR transmittances are very weak (10% at maximum), confirming the small rate of reaction already suggested from the electronic spectra. Monomeric  $H_2O$  is always present, with a sharp absorption band at 1615 cm<sup>-1</sup>, but no additional bands due to  $M(H_2O)$  complexes have been observed, as described by Hauge and co-workers,<sup>24</sup> except for the Fe/CO<sub>2</sub> system which

TABLE V: IR Band Frequencies Observed for Ti/CO<sub>2</sub>/Ar, Ti/ $^{13}$ CO<sub>2</sub>/Ar, and Ti/C<sup>18</sup>O<sub>2</sub>/Ar Deposits (Ti/CO<sub>2</sub> ~ 1/1000, CO<sub>2</sub>/Ar ~ 1/10) after Annealing up to 40 K

IR fr	eq, cm <sup>-1</sup> ( $\Delta \bar{\nu}$	, cm <sup>-1</sup> )	
$CO_2/Ar$	<sup>13</sup> CO <sub>2</sub> /Ar	$C^{18}O_2/Ar$	assignments
2145	2095 (50)	2090 (55)	$\nu(C \equiv O)$ (carbon monoxide)
1730	1685 (45)	1700 (30)	$\nu(C=O)$
1185	1165 (20)	1140 (45)	$\nu(C-O)$
985	985 (0)	945 (40)	"(Ti=0)
950	950 (0)	910 (40)∫	<i>v</i> (11=0)
895	895 (0)	895 (0)	?
455	455 (0)	445 (10)	$\nu$ (Ti–O)
1615	1615 (0)	1615 (0)	$\delta(H_2O)$

gives rise to an absorption band at 1565 cm<sup>-1</sup> close to the 1563-cm<sup>-1</sup> band of  $Fe(H_2O)$  complex.

No absorption bands are detected in the low-frequency range  $(\bar{\nu} \leq 500 \text{ cm}^{-1})$  as well as in diluted matrices  $(CO_2/Ar = 1/10)$  at 15 K. Upon annealing to 40 K, the diluted matrices produce the same spectra as in neat matrices at 15 K, except for Ti and Cu, for which different spectra are obtained.

Annealing neat  $M/CO_2$  matrices up to 60 K generally leads to the complete disappearance of the IR spectra observed at 15 K with no new bands being detected during warm-up: this indicates that most complexes are thermally unstable and simply decompose. However, Fe and Ni complexes, upon annealing above 80 K, do give rise to new spectral features.

The results with respect to dilution in argon and thermal activation indicate that only a single complex with  $CO_2$  is formed for each system. Finally a survey of the IR spectra obtained allows us to divide all the studied metals into four groups, according to their absorption ranges:

(1) oxophile metals (Ti, V, Cr) with three major bands in the 1750-1690-, 1180-1090-, and 1000-930-cm<sup>-1</sup> ranges;

(2) Fe and Co, with two major bands in the 1630–1560- and 1210-1190-cm<sup>-1</sup> regions;

(3) Ni, with bands at very high frequencies, 1850-1815 cm<sup>-1</sup>, and other absorptions at 1131 and 744 cm<sup>-1</sup>;

(4) Cu, with three bands at 1716, 1215, and 718  $cm^{-1}$ .

As isotopic experiments have been carried out on Ti, Fe, and Cu compounds, we present now the detailed results obtained for these three metals; then, a following section will be devoted to a discussion of the four groups as defined above.

2.2.1. Reactions of Ti with  $CO_2$ . The infrared spectrum resulting from condensation of Ti atoms with pure  $CO_2$  at 15 K is shown in Figure 4a. We observe three main groups of bands at 1776 (sh)-1735 (vs), 1147 (sh)-1132 (mbr), and 988 (sh)-955 (s) cm<sup>-1</sup> and we also note the presence of weak bands at 2138, 2100 (br), 1946, 895, and 885 cm<sup>-1</sup>.

When annealing up to 53 K (see Figure 4b), the broad band at 2100 cm<sup>-1</sup> becomes structured with sharp maxima at 2110, 2089, and 2079 cm<sup>-1</sup>; the band at 1735 cm<sup>-1</sup> is shifted to 1743 cm<sup>-1</sup>, that at 988 cm<sup>-1</sup> increases, and those at 895 and 885 cm<sup>-1</sup> vanish. When the temperature is increased above 80 K, all the bands gradually disappear.

Condensation reactions of titanium atoms with  $CO_2/N_2$  (1/1) mixtures lead to similar results and we do not observe additional or increased band intensities.

Condensation experiments with  $CO_2/O_2$  (3/1) mixtures (see Figure 4c) lead to the disappearance of absorptions at 2138, 2110,

<sup>(24)</sup> Kauffman, J. W.; Hauge, R. H.; Margrave, J. L. J. Phys. Chem. 1985, 89, 3541, 3547.



Figure 6. IR spectra of reaction products of iron atoms with  ${}^{13}CO_2$  (a),  $CO_2/{}^{13}CO_2$  (b),  $C{}^{18}O_2$  (c), and  $CO_2/{}^{18}O_2$  (d) at 15 K.

TABLE VI: Frequencies  $\nu$  and Isotopic Shifts  $\Delta \bar{\nu}$  Observed for Fe Deposits with CO<sub>2</sub>, <sup>13</sup>CO<sub>2</sub>, and C<sup>18</sup>O<sub>2</sub> at 15 K

IR				
$\overline{\rm CO_2/Fe}$	<sup>13</sup> CO <sub>2</sub> /Fe	$C^{18}O_2/Fe$	assignments	
1615	1615 (0)	1615 (0)	$\delta(H_2O)$	
1565	1525 (40)	1540 (25)	$\nu_a(OCO)$	
1210	1185 (25)	1172 (38)	$\nu_{\rm s}({\rm OCO})$	
	IR CO <sub>2</sub> /Fe 1615 1565 1210	$\begin{tabular}{ c c c c c c } \hline IR freq, cm^{-1} (\Delta \bar{\nu}, \\ \hline CO_2/Fe & {}^{13}CO_2/Fe \\ \hline 1615 & 1615 (0) \\ 1565 & 1525 (40) \\ 1210 & 1185 (25) \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c c } \hline & IR freq, cm^{-1} (\Delta \overline{\nu}, cm^{-1}) \\ \hline & CO_2/Fe & {}^{13}CO_2/Fe & C^{18}O_2/Fe \\ \hline & 1615 & 1615 (0) & 1615 (0) \\ \hline & 1565 & 1525 (40) & 1540 (25) \\ \hline & 1210 & 1185 (25) & 1172 (38) \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

2089, 2079, and 1946 cm<sup>-1</sup>; the band at 988 cm<sup>-1</sup> is now stronger than that at  $955 \text{ cm}^{-1}$ ; new absorption bands appear at 1552, 1040, and 998 cm<sup>-1</sup>.

In neat O<sub>2</sub> matrices (see Figure 4d), the infrared spectrum exhibits clear absorptions at 1548 (m), 1040 (m), 998 (s), 954 (w), and 805 (w) cm<sup>-1</sup>, which are respectively due to  $\nu(O_2)$  and the stretching modes  $\nu(O-O)$  or  $\nu(Ti=O)$  of some titanium-oxygen complexes. Isotopic experiments with <sup>13</sup>CO<sub>2</sub> and C<sup>18</sup>O<sub>2</sub> lead to the frequency shifts reported in Table IV. The shifts of the band at 2138 cm<sup>-1</sup> to 2089 (<sup>13</sup>CO<sub>2</sub>) and to 2085 (C<sup>18</sup>O<sub>2</sub>) cm<sup>-1</sup> show that this absorption is due to some carbon monoxide isolated in the CO<sub>2</sub> matrix as a result of the reduction of CO<sub>2</sub>.

Doublet intensity patterns (see Figure 5) observed in the mixed  ${}^{12}CO_2/{}^{13}CO_2/{}^{Ti}$  and  $C^{16}O_2/C{}^{18}O_2/{}^{Ti}$  deposits demonstrate the 1:1 stoichiometry of these compounds (one CO<sub>2</sub> molecule per titanium atom).

The lack of isotopic effects in the presence of  ${}^{13}\text{CO}_2$  and the doublet patterns observed with  $\text{CO}_2/\text{C}{}^{18}\text{O}_2/\text{Ti}$  matrices on the bands at 988 and 955 cm<sup>-1</sup> provide evidence that these bands are due to Ti=O bonds. From results of annealing and isotopic experiments, we thus conclude that several compounds exist in the matrix: CO, Ti(CO)<sub>n</sub>, Ti(O), and Ti(O)(CO)(CO<sub>2</sub>).

Titanium atoms do not react with  $CO_2/Ar$  (1/10) mixtures at 15 K but lead to a similar spectrum after annealing up to 40 K, with frequencies shifted to 2145, 1730, 1190, 985, 950, 895, and 455 cm<sup>-1</sup>. No bands due to titanium carbonyls were detected. The <sup>13</sup>CO<sub>2</sub> and C<sup>18</sup>O<sub>2</sub> shifts are different from those observed in neat CO<sub>2</sub> matrices. The respective frequencies are reported in Table V and will be discussed in the next section. However, we conclude that the diluted Ti/CO<sub>2</sub>/Ar matrix contains, after annealing to 40 K, only the following compounds: CO, Ti(O), and Ti(O)(CO<sub>2</sub>).

2.2.2. Reactions of Fe with  $CO_2$ . Atomic iron reacts with  $CO_2$  by cocondensation at 15 K and gives rise to infrared peaks at 1565 and 1210 cm<sup>-1</sup>. No free CO nor iron carbonyls are detected in



Figure 7. IR spectra of a Fe/CO<sub>2</sub> (1/1000) deposit at 15 K and annealed to 50, 60, 70, 80, and 95 K.



Figure 8. IR spectra of Cu/CO<sub>2</sub> (a), Cu/CO<sub>2</sub>/C<sup>18</sup>O<sub>2</sub> (b), and Cu/CO<sub>2</sub>/ $^{13}CO_2$  (c) deposits at 15 K.

our infrared experiments, but monomeric isolated  $H_2O$  is observed at 1615 cm<sup>-1</sup>.

Both peaks at 1565 and 1210 cm<sup>-1</sup> exhibit significant carbon-13 and oxygen-18 dependence and are thus both assigned to the stretching modes of a bent CO<sub>2</sub> complexed molecule rather than to the Fe(H<sub>2</sub>O) adduct which has an infrared absorption at 1563 cm<sup>-1</sup>. In Fe/<sup>12</sup>CO<sub>2</sub>/<sup>13</sup>CO<sub>2</sub> and Fe/C<sup>16</sup>O<sub>2</sub>/C<sup>18</sup>O<sub>2</sub> mixed matrices, one observes 1:1 doublet patterns, a result consistent with species containing one CO<sub>2</sub> molecule per metallic atom. The infrared spectra are shown in Figure 6; the corresponding band wavenumbers and tentative assignments are listed in Table VI.

Annealing of a Fe/CO<sub>2</sub> matrix induces a growing of the band intensities up to 60 K; in contrast, above 60 K, these bands decrease and simultaneously new bands appear at 1882, 1867 and 882, 865 cm<sup>-1</sup>. These bands must be assigned to bridged iron carbonyls and to iron oxide modes (see Figure 7).

2.2.3. Reactions of Cu with CO<sub>2</sub>. After deposition at 15 K, the infrared spectrum exhibits bands at 2138 (m), 1722 (sh), 1716 (s), 1615 (m), 1411 (vw), 1343 (vw), 1215 (m) and 718 (mw)  $cm^{-1}$ .

Upon annealing up to 80 K, the bands at 1722, 1716, 1215, and 718 cm<sup>-1</sup> increase together; they decrease above 80 K. All other absorptions vanish and no new band is detected.

In isotopic experiments with  ${}^{13}CO_2$  and  $C{}^{18}O_2$  the bands at 2138, 1722, 1716, and 1215 cm<sup>-1</sup> are shifted to lower frequencies; they are respectively assigned to carbon monoxide and to a coordinated CO<sub>2</sub> molecule. Bands at 1411, 1343, and 718 cm<sup>-1</sup> were not detected in isotopic experiments; the band at 1615 cm<sup>-1</sup> has no isotopic effect: it is due to isolated H<sub>2</sub>O in the matrix.

The deposition using  ${}^{13}CO_2/Ar$  matrix leads to an infrared spectrum without any absorptions arising from a complex; however after annealing up to 37 K, it exhibits major bands at 1638, 1228, and 723 cm<sup>-1</sup>, slightly shifted from those early observed at 15 K in a neat  ${}^{13}CO_2$  matrix: 1672, 1205 cm<sup>-1</sup>. So, as previously encountered for titanium, a Cu/CO<sub>2</sub> dilution in argon, followed by argon evaporation, does not lead to the same M(CO<sub>2</sub>) system as observed in the pure CO<sub>2</sub> matrix. Figure 8 shows the infrared spectrum of Cu/CO<sub>2</sub> and the doublet patterns obtained in mixed  ${}^{12}CO_2/{}^{13}CO_2$  and  $C^{16}O_2/C^{18}O_2$  matrices, which are again char-

TABLE VII: Infrared Frequencies Observed for Cu Deposits in Pure CO<sub>2</sub>,  $^{12}CO_2$ , and  $C^{18}O_2$  Matrices at 15 K and Tentative Assignments

IR freq			
CO <sub>2</sub> /Cu	<sup>13</sup> CO <sub>2</sub> /Cu	$C^{18}O_2/Cu$	assignments
2138	2089 (49)	2084 (54)	$\nu(C \equiv 0)$ in CO
1722, 1716 (s)	1672 (44)	1687 (29)	$\nu(C==O)$
1615	1615 (0)	1615 (0)	$\delta(H_2O)$
1411	а	а	carbonates
1343	а	а	carbonates
1215	1205 (10)	1166 (49)	$\nu(C-O)$
718	а	а	$\delta(OCO)$
	IR freq CO <sub>2</sub> /Cu 2138 1722, 1716 (s) 1615 1411 1343 1215 718	$\begin{tabular}{ c c c c c c c } \hline IR freq, cm^{-1} (\Delta\bar{\nu}, cm \\ \hline CO_2/Cu & {}^{13}CO_2/Cu \\ \hline 2138 & 2089 (49) \\ 1722, 1716 (s) & 1672 (44) \\ 1615 & 1615 (0) \\ 1411 & a \\ 1343 & a \\ 1215 & 1205 (10) \\ 718 & a \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$

"Not observed in labeled matrices.

TABLE VIII: Frequencies and Isotopic Shifts of  $\nu(C=0)$  and  $\nu(C=0)$  Vibrations in Known CO<sub>2</sub> Complexes, According to the Structure of the Complex

complexes	<i>v</i> , cm <sup>-1</sup>	Δi	$\bar{\nu}(^{13}CO_2),$ cm <sup>-1</sup>	Δ;	$\frac{\overline{\nu}(C^{18}O_2)}{cm^{-1}}$
$LiCO_2(C_s)$	1751	44		33	
			$\Sigma = 61$		$\Sigma = 74$
end-on coord <sup>7</sup>	1221	17		41	
$[(pr-salen)Co(CO_2)]^- K^+$	1650	40			
			$\sum = 70$	а	
$C \text{ coord}^{11}$	1280	30			
$(PCy_3)_2Ni(CO_2)$	1728	43		33	
side-on coord <sup>13</sup>	1172	13	$\sum = 56^{b}$	23	$\sum = 56^b$

<sup>a</sup> Unknown. <sup>b</sup> Our work, in collaboration with M. Aresta.

acteristic of 1:1  $CuCO_2$  complexes. Wavenumbers and tentative assignments are listed in Table VII.

#### **IV.** Discussion

According to the electronic spectroscopy results, we know that no metallic aggregates are present in the matrices, that  $CO_2$ spontaneously reacts with transition-metal atoms at 15 K with a very weak rate of reaction, and that charge-transfer transitions in MCO<sub>2</sub> complexes are located in the UV energy range. Similar results were reached by Ozin et al.<sup>17</sup> for the UV-visible spectra of AgCO<sub>2</sub> (248, 286, 340, 404 nm) and AuCO<sub>2</sub> (240, 260, 310, 394 nm).

Infrared spectra confirm the low yield of reaction of transition-metal atoms toward  $CO_2$  since the most intense bands equal approximately 10% absorption. Also it was not easy to observe the IR absorptions of new molecules due to very small interactions with  $CO_2$  since they lie close to the huge bands of  $CO_2$  which has been used pure and in high concentration in argon matrices.

All the observed frequencies are in the ranges expected for  $CO_2$  complexes, as shown in Table I, where we have collected the vibrational frequencies found in the literature for different metallic  $CO_2$  compounds. For  $CO_2$  complexes with inequivalent O atoms (end-on and side-on structures), absorptions are lying in the 1780–1620- and 1300–1100-cm<sup>-1</sup> ranges, whereas in C-coordinated  $CO_2$  complexes, with two equivalent O atoms, the two stretching  $\nu(CO)$  modes are expected closer in the 1650–1550- and 1280–1180-cm<sup>-1</sup> regions.

If infrared band wavenumbers alone do not allow to discriminate between C-coordinated, side-on, and end-on  $CO_2$  complexes, the situation is more favorable if we look at the isotopic shifts of the stretching modes (and of the bending mode when it is observed), using <sup>13</sup>C and <sup>18</sup>Ø. The only published isotopic results for  $CO_2$ complexes with already known structures are those of LiCO<sub>2</sub><sup>7</sup> and of [(pr-salen)Co(CO<sub>2</sub>)]<sup>-</sup>K<sup>+11</sup> complexes (see Table VIII). It seems interesting to extend such a study. In that way, the isotopic shifts have been recently measured in our laboratory for (PCy<sub>3</sub>)<sub>2</sub>Ni(CO<sub>2</sub>)<sup>13</sup> (work in collaboration with Professor Aresta). So structural conclusions will be based on the isotopic shifts observed in the infrared spectra. Furthermore, these isotopic studies lead us to propose schematic pathways for the low-temperature reactions  $M + CO_2$  typical of each metal group: oxophiles, iron, cobalt, nickel, and copper. 1.  $CO_2$  Complexes of Ti, V, and Cr. We have already seen that condensation of Ti atoms in pure  $CO_2$  leads to the formation of (O)(CO)Ti(CO<sub>2</sub>). The comparison of observed isotopic shifts with those listed in Table VIII shows that the compound cannot have an end-on or a C-coordinated structure.

A preliminary IR study of the complex  $Mo(PMe_3)_4(CO_2)_2$ isotopically enriched with 50%  $^{13}CO_2$ , provided by E. Carmona, reveals that the stoichiometry of this 1-2 complex cannot be achieved by analysis of the  $\nu(C=O)$  vibrations as they are uncoupled between the two  $CO_2$  molecules. In contrast, the  $\nu(C=O)$ and  $\delta(OCO)$  modes present the expected triplet structure of a dimer complex.

Since we only observe a doublet pattern for all the observed stretching modes  $\nu(C=0)$ ,  $\nu(C=0)$ ,  $\nu(C=0)$ , and  $\nu(T=0)$  with  $C^{18}O_2$ , a complex with one  $CO_2$  molecule is formed. Furthermore, the sum of the isotopic shifts on  $\nu(C=0)$  and  $\nu(C=0)$  absorptions (respectively 45 and 57 cm<sup>-1</sup> for C-13 and O-18) is close to those measured in  $(PCy_3)_2Ni(CO_2)$  (56 cm<sup>-1</sup> for C-13 and O-18 (see Tables IV and VIII)). We thus propose the following reactivity pathway:



Light irradiation with a Hg lamp leads to the decomposition of the complex 1. Annealing up to 80 K leads to formation of the very similar complex 1a with three bands at 1740, 1150, and 980 cm<sup>-1</sup>, respectively assigned to the  $\nu$ (C=O),  $\nu$ (C-O), and  $\nu$ (Ti=O) modes.



Some similar reaction schemes have been proposed by Almond<sup>25</sup> and Poliakoff<sup>26</sup> for W and Cr atoms in  $CO_2/O_2$  matrices.

In diluted matrices, isotopic shifts can be compared with those of  $LiCO_2$ : 61 and 74 cm<sup>-1</sup> versus 65 and 75 cm<sup>-1</sup> for Ti-C-13 and O-18, respectively (see Tables V and VIII). No titanium carbonyls are detected. Thus we propose an end-on structure with the following reactional scheme:

$$Ti + CO_2 \xrightarrow{Ar. 15 \text{ K}} [Ti - O - C^{-0}]^* \longrightarrow Ti = 0 + CO$$
  
not obsd  
$$0 = Ti - O - C^{-0}$$

<sup>(25)</sup> Almond, M. J.; Dows, A. J.; Perutz, R. N. Inorg. Chem. 1985, 24, 275.

<sup>(26)</sup> Poliakoff, M.; Smith, K. P.; Turner, J. J.; Wilkinson, A. J. J. Chem. Soc., Dalton Trans. 1982, 651.

It appears that the nature of the matrix plays an important role in the determination of the most stable structure of the  $CO_2$ complexes. It also appears that Ti can coordinate  $CO_2$  only after initially reacting with a  $CO_2$  molecule.

By comparison of the infrared spectra, we propose for V and Cr analogous chemical behavior, i.e., oxidation followed by complexation with  $CO_2$ . But it is probable that V has a higher oxidation number than Ti when it coordinates CO<sub>2</sub> (a high frequency is observed for the carbonyl stretching at 2160 cm<sup>-1</sup>) although, with Cr, no metal carbonyls are detected.

2. CO<sub>2</sub> Complexes of Fe and Co. From the observed IR frequencies and isotopic shifts, Fe atoms probably form C-coordinated

complexes in neat CO<sub>2</sub> matrices (see Tables VI and VIII).

If the molecule possesses  $C_{2v}$  symmetry, the gap between  $v_a$ -(OCO) and  $\nu_s(OCO)$  is related to the value of the OCO angle. Thus, we expect for CoCO<sub>2</sub> ( $\Delta \nu = 435 \text{ cm}^{-1}$ ) a larger angle than for FeCO<sub>2</sub> ( $\Delta \nu = 355 \text{ cm}^{-1}$ ).

A more interesting point for Fe is its apparent ability to reduce  $CO_2$  to CO by thermal activation of the  $CO_2$  matrix (see Figure 7). This may occur by the following reaction scheme:

3. CO<sub>2</sub> Complexes of Ni. The infrared spectrum displays new absorptions (see Figure 9) due to coordinated  $CO_2$ . Bands exhibit multiplet structures at 1850 (sh), 1818 (s), 1812 (s), 1734 (sh) cm<sup>-1</sup> due to  $\nu$ (C=O), at 1170 (w), 1131 (m) cm<sup>-1</sup> due to  $\nu$ (C-O) and at 744 (m) cm<sup>-1</sup> due to  $\delta$ (OCO). The multiplet structure indicates that slightly different complex structures exist in the matrix perhaps due to slightly different matrix sites which do not anneal away.

Another interesting result with Ni (as with Fe) is its ability to reduce CO<sub>2</sub> to CO by annealing the matrix up to 106 K. Figure 9 shows the infrared spectra obtained at 15 and 106 K. As evidenced by the high-frequency values at 106 K ( $\nu$ (CO) = 2050 cm<sup>-1</sup>), the annealing of the matrix leads to aggregation of Ni atoms and to the formation of linear nickel carbonyls NirCO and nickel oxide ( $\nu = 750 \text{ cm}^{-1}$ ) by decomposition of the NiCO<sub>2</sub> complex.

Dilution in argon gives no spectrum at 15 K, and the same spectrum as in neat CO<sub>2</sub> after annealing up to 40 K, a result in agreement with the existence of only one stoichiometry, probably 1:1 by analogy with other metals.

The high  $\nu(C==O)$  frequency values (around 1815 cm<sup>-1</sup>) allow us to exclude the formation of a C-coordinated NiCO<sub>2</sub> complex.

4. CO<sub>2</sub> Complexes of Cu. Frequency values, isotopic shifts, and doublet patterns obtained in mixed matrices allow us to conclude that in neat CO<sub>2</sub>, Cu atoms form 1:1 complexes, probably with an end-on structure, as indicated by the values of the isotopic shifts. Comparison of Tables VII and VIII shows that both the breakdown of the shifts and their sums for C-13 and O-18 for the  $CuCO_2$  complex are highly similar to those of the LiCO<sub>2</sub> (Cs) compound, for which the end-on geometry has been proposed by Hauge.<sup>7</sup> A small part of  $CO_2$  is also reduced on the hot filament, since free CO is detected in the infrared spectrum at 2138  $cm^{-1}$ .

In order to determine the structure of this complex, some ab initio calculations have been carried out by Caballol et al.<sup>27</sup> Four geometries were tested: end-on, side-on, C-coordinated, and O,O-coordinated (ionic  $C_{2v}$  complex A).



Apart from the side-on bonded  $Cu(CO_2)$  which may be formulated as a weakly bound van der Waals-type complex, only the end-on

The Journal of Physical Chemistry, Vol. 92, No. 8, 1988 2183



Figure 9. IR spectra of Ni/CO<sub>2</sub> deposit at 15 K and after annealing up to 110 K (M/CO<sub>2</sub> ~ 1/1000).

complex is found to be stable with respect to  $Cu + CO_2$  fragments. It is characterized by an important charge transfer from copper to  $CO_2$  with the unpaired electron located at the carbon atom. It is predicted to have  $C_s$  symmetry and a bent geometry (cis form):

This result is in agreement with our conclusions, although we cannot discuss the values of the angles.

#### V. Normal-Coordinate Analysis

Normal-coordinate analysis is generally used to check the experimental conclusions. This implies the knowledge of a relevant initial force field and an extensive set of experimental data which is not available here.

However, no normal-coordinate analysis has been yet performed on CO<sub>2</sub>-transition-metal complexes and some calculations about LiCO<sub>2</sub> systems<sup>7</sup> have been discussed in respect to large interactions used to obtain a good fit.28

We have performed quantitative treatment for FeCO<sub>2</sub>, CuCO<sub>2</sub>, and the two geometrical isomers of OTiCO<sub>2</sub> assuming the most probable geometries from anterior structural analysis on similar systems (see indicated references).

Our aims were (i) to give an approximate value of the force constants in these complexes, and (ii) to analyze the order of magnitude of the isotopic shifts C-13 and O-18 as a function of the geometry of the coordinated  $CO_2$  moiety.

The main results are summarized in Table IX. Compared with the free molecule, the force constants of coordinated  $CO_2$  have significantly decreased (-50%). Good fits are obtained for frequencies and isotopic shifts only when OCO angle is far away from 180° (typically between 120 and 150°).

Keeping in mind that a reduced set of interaction force constants has been used, we have obtained good fits for C-coordinated and end-on complexes, although the force field (and experimental data) must still be improved for side-on structures, because of the presence of a metallic cycle



The strategy adopted to improve our side-on models involves calculating force constants for the structurally already known side-on complexes  $(PCy_3)_2Ni(CO_2)^{13}$  and  $(PMe_3)_4Mo(CO_2)_2^{29}$ and transferring these values to our compounds. The syntheses of these isotopically labeled species are still in progress in our

<sup>(27)</sup> Caballol, R.; Sanchez-Marcos, E.; Barthelat, J. C. J. Phys. Chem. 1987. 91. 1328.

 <sup>(28)</sup> Manceron, L. Thèse 3e cycle, Université de Paris VI, 1983.
 (29) Alvarez, R.; Carmona, E.; Marin, J. M.; Poveda, M. L.; Guttierez-

<sup>Puebla, E.; Monge, A. J. Am. Chem. Soc. 1986, 108, 2286.
(30) Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed.; Wiley: New York, 1986.</sup> 

TABLE IX: Comparison of Observed and Calculated Frequencies (cm<sup>-1</sup>) for FeCO<sub>2</sub> (C<sub>2v</sub>), CuCO<sub>2</sub> (C<sub>s</sub> End On), and OTiCO<sub>2</sub> (C<sub>s</sub> End On)<sup>a</sup>

	MCO <sub>2</sub>		$\Delta \overline{\nu}(1)$		$\Delta \overline{\nu}(C^{10}O_2)$				
complex	obsd	calcd	obsd	calcd	obsd	calcd	force constants		
FeCO <sub>2</sub>	1565 (v <sub>a</sub> )	1559	40	44	25	23	$k_{C=O} = 8.5, k_{FeC} = 4.5, k_{OCO} = 1, k_{FeCO} = 0.85, k_{CO,CO} = 1.85, k_{CO,OCO} = 0.44, k_{CO,FeC} = 0.64$		
	$1210 (\nu_s)$	1238	25	21	38	39			
CuCO <sub>2</sub>	1716 (v <sub>C=0</sub> )	1724	44	47	29	29	$k_{C=0} = 10.0, k_{C=0} = 8.5, k_{Cu0} = 1.6, k_{OC0} = 1.07, k_{Cu0C} = 0.35, k_{C0,C0} = 1.3, k_{C0,OC0} = 0.4, k_{C0,Cu0C} = 0.38$		
	$1215 (v_{CO})$	1208	10	10	49	52			
	718 $(\delta_{OCO})$	720		14		22			
OTiCO <sub>2</sub>	1730 (v <sub>C=0</sub> )	1745	45	44	30	34	$k_{\text{C}-\text{O}} = 11.6, k_{\text{C}-\text{O}} = 6.0, k_{\text{T}i-\text{O}} = 1.6, k_{\text{T}i-\text{O}} = 6.3, k_{\text{OCO}} = 1.15, k_{\text{T}i\text{OC}} = 0.35, k_{\text{O}-\text{T}i\text{O}} = 0.35, k_{\text{O}-\text{T}i\text{O}} = 0.35, k_{\text{O}-\text{O}} = 1.0, k_{\text{CO},\text{OO}} = -0.35, k_{\text{O}-\text{T}i\text{O}} = 0.4$		
	1185 ( $\nu_{CO}$ )	1187	20	20	50	38			
	950 $(v_{Ti=0})$	952	0	0	40	39			
	455 $(\nu_{\rm TiO})$	313	0	0	10	10			

<sup>a</sup> Force constants are given in mdyn  $Å^{-1}$  for bonds, mdyn Å rad<sup>-2</sup> for angles, and mdyn rad<sup>-1</sup> for bond-angle interactions.

laboratory in collaboration with Professors M. Aresta and E. Carmona.

## VI. Conclusion

The experimental results of the present work lead us to conclude that the first examples of binary transition-metal-atom-carbon dioxide complexes have been observed and can be formulated as firmly bound  $M(CO_2)$  compounds for the following reasons:

UV-visible spectra are consistent with a spontaneous reaction between transition-metal atoms and  $CO_2$  at 15 K.

Characteristic FTIR spectra are observed at 15 K: only one kind of compound is formed in both diluted and pure matrices, except for Ti and Cu atoms.

Data obtained in mixed labeled matrices  $({}^{12}C/{}^{13}C \text{ and } {}^{16}O/{}^{18}O)$  suggest that the 1:1 stoichiometry is predominant in all cases.

From infrared data, the Cu complex probably has an end-on  $C_s$  geometry whereas FeCO<sub>2</sub> seems to be a C-coordinated  $C_{2v}$  compound.

Oxophile metals (Ti, V, Cr) are oxidized by fixation of oxygen atom coming from the cleavage of the first  $CO_2$  coordinated molecule and are bound to a second  $CO_2$  molecule possibly in a side-on or end-on fashion.

Fe and Ni atoms are able to reduce  $CO_2$  to CO when annealing complexes  $M(CO_2)$  up to 80 and 106 K, respectively. The corresponding reaction schemes probably involve aggregation processes.

Acknowledgment. We are pleased to acknowledge fruitful discussions with Professors M. Aresta and E. Carmona about  $CO_2$  chemistry, Dr. J. P. Malrieu about theoretical ab initio calculations on the CuCO<sub>2</sub> complex, and Dr. C. Sourisseau for a critical reading of the manuscript. We thank the NATO for support (grant RG 109.82 to M.T.).

**Registry No. 1**, 113220-84-1; **1a**, 113220-85-2; Ti, 7440-32-6; V, 7440-62-2; Cr, 7440-47-3; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0; Cu, 7440-50-8; CO<sub>2</sub>, 124-38-9; Ti(O), 12137-20-1; CoCO<sub>2</sub>, 113220-86-3; FeCO<sub>2</sub>, 113220-87-4; CuCO<sub>2</sub>, 68868-29-1; Ti(O)(CO<sub>2</sub>), 113220-88-5; nickel oxide, 11099-02-8.

# Factors Affecting Gas-Phase Continuous Wave Infrared Laser Sensitized Pyrolysis

# Jianzhong Zhu and Edward S. Yeung\*

Ames Laboratory–USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011 (Received: May 6, 1987; In Final Form: October 19, 1987)

A model is developed for predicting temperature profiles in a gas cell containing an absorbing gas when irradiated by a CW laser beam with well-defined parameters. The model takes into account the explicit temperature dependence of heat capacities, thermal conductivities, molar absorptivities, and gas densities. The predicted transmittance of the laser beam as a function of incident power agrees with experimental values. The model is further used to predict rate parameters of a standard homogeneous pyrolysis reaction that is sensitized by the heated gas. The results provide insight into the comparison between the traditional thermal processes and CW laser sensitized pyrolysis.

The use of lasers for inducing chemical reactions is a mature field.<sup>1</sup> One application involves the excitation of gaseous reactants by an infrared laser, with or without a sensitizer. Of interest is the comparison with traditional thermal reactions, since the hot reactants can be generated by a laser away from the walls of the cell, avoiding contributions from hot surfaces. Even though the early work on homogeneous pyrolysis by Shaub and Bauer<sup>2</sup> is based on a CW infrared laser and a sensitizer, much more work has been done using pulsed infrared lasers.<sup>3</sup> The latter approach even allows direct pumping of the reactant in the absence of a sensitizer. While very often the laser-induced reactions are shown to closely parallel thermal reactor or shock tube results,<sup>2,3</sup> there are also examples of significant differences in rate parameters and branching ratios in these studies.<sup>4</sup>

<sup>(1)</sup> Steinfeld, J. I., Ed. Laser-Induced Chemical Processes; Plenum: New York, 1981.

<sup>(2)</sup> Shaub, W. M.; Bauer, S. H. Int. J. Chem. Kinet. 1975, 7, 509.

<sup>(3) (</sup>a) Tsang, W.; Walker, J. A.; Braun, W. J. Phys. Chem. 1982, 86, 719.
(b) Dai, H.-L.; Specht, E.; Berman, M. R.; Moore, C. B. J. Chem. Phys. 1982, 77, 4494.

<sup>(4) (</sup>a) McMillen, D. F.; Lewis, K. E.; Smith, G. P.; Golden, D. M. J. Phys. Chem. 1982, 86, 709. (b) Moylan, C. R.; Brauman, J. I. Int. J. Chem. Kinet. 1986, 18, 379. (c) Berman, M. R.; Comita, P. B.; Moore, C. B.; Bergman, R. G. J. Am. Chem Soc. 1980, 102, 5692. (d) Comita, P. B.; Berman, M. R.; Moore, C. B.; Bergman, R. G. J. Phys. Chem. 1981, 85, 3266.