Specific Intermolecular Interaction of Carbon Dioxide with Polymers

Sergei G. Kazarian, Michael F. Vincent, Frank V. Bright,[†] Charles L. Liotta, and Charles A. Eckert*

Contribution from Schools of Chemical Engineering and Chemistry and Specialty Separations Center, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Received February 6, 1995[⊗]

Abstract: Fourier transform IR spectroscopy has been used to investigate the interaction of carbon dioxide with polymers. IR transmission and attenuated total reflectance spectra were obtained for CO_2 impregnated into polymer films. It has been shown that the polymers possessing electron-donating functional groups (e.g., carbonyl groups) exhibit specific interactions with CO_2, most probably of Lewis acid−base nature. An unusual aspect is the use of the bending mode (ν_2) of CO_2 to probe polymer−CO_2 interactions. The evidence of the interaction is the observation of the splitting of the band corresponding to the CO_2 ν_2 mode. This splitting indicates that the double degeneracy of the ν_2 mode is removed due to the interaction of electron lone pairs of the carbonyl oxygen with the carbon atom of the CO_2 molecule. This splitting has not been observed for polymers lacking electron-donating functional groups (e.g., poly(ethylene)). In contrast, the ν_3 mode shows little if any sensitivity to this interaction, which is in accordance with the interaction where CO_2 molecule acts as an electron acceptor. Finally, the chemical and engineering implications of this type of specific interaction of CO_2 with polymers are discussed; perhaps the changes in spectra of CO_2 incorporated into polymers might serve as a basis for prediction of the solubility of CO_2 in polymers.

Introduction

Supercritical carbon dioxide ($scCO_2$) has tremendous potential for the modification and processing of polymers.[1,2] Previous studies in this area have used $scCO_2$ for separations, extraction, and fractionation,[1,3] for swelling and sorption,[4−8] for polymer impregnation,[6,9,10] as a medium for polymer synthesis,[11,12] for polymer precipitation by expansion from supercritical solution,[13] and for polymerization reactions within CO_2-swollen polymers.[14] Other recent work has centered on the ability of $scCO_2$ to lower the glass transition temperature and plasticize polymers[8,15,16] and modeling of this phenomena.[7,8,15,17]

Despite numerous studies of polymers with gases or supercritical fluids, there is a dearth of molecular level information on interactions within these polymer systems. As a result, there is now the general perception that polymer swelling or gas sorption is a purely *physical* phenomena, not a result of specific chemical interactions between the gas/fluid and the polymer.

Infrared (IR) spectroscopy is an excellent tool to probe such interactions; it has been used to study intermolecular interactions in supercritical fluid[18−21] and even to probe polymer films subjected to high-pressure CO_2.[22−25] However, no evidence for

---

[†] On sabbatical leave from Department of Chemistry, Natural Sciences and Mathematics Complex, State University of New York at Buffalo, Buffalo, NY 14260-3000.

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

(1) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice,* 2nd ed.; Butterworth-Heinemann: Boston, MA, 1994.

(2) (a) Koros, W. J. Barrier polymers and structures. *ACS Symp. Ser.* **1989**, *423*. (b) Vieth , W. R. *Diffusion In and Through Polymers, Principles and Applications*; Hanser Werlag: Munich, 1991. (c) van Krevelen, D. W. *Properties of Polymers*; Elsevier: New York, 1990. (d) Koros, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1611−1628. (e) Chiou, J. S.; Paul, D. R., *J. Memrane Sci.* **1989**, *45*, 167−189. (f) Wessling, M.; Mulder, M. H. V.; Bos, A.; van der Linden, M.; Bos, M.; van der Linden, W. E. *J. Membrane Sci.* **1994**, *86*, 193−198.

(3) Paulaitis, M. E.; Krukonis, V. J.; Reid, R. C. *Rev. Chem. Eng.* **1983**, *1*, 179.

(4) (a) Wissinger, R. G.; Paulaitis, M. E. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 2497−2510. (b) Wissinger, R. G.; Paulaitis, M. E. *J. Polym. Sci., Part B : Polym. Phys.* **1991**, *29*, 631−633.

(5) Kiamos, A. A.; Donohue, M. D. *Macromolecules* **1994**, *27*, 357−364.

(6) Berens, A. R.; Huvard, G. S.; Korsmeyer, R. W.; Kunig, F. W. *J. Appl. Polym. Sci.* **1992**, *46*, 231−242.

(7) (a) Goel, S. K.; Beckman, E. J. *Polym. Eng. Sci.* **1994**, *34*, 1137−1147. (b) Goel, S. K.; Beckman, E. J. *Polym. Engr. Sci.* **1994**, *34*, 1148−1156.

(8) Berens, A. R.; Huvard, G. S. In *Supercritical Fluid Science and Technology*; Johnston, K. P, Penninger, J. M. L., Eds.; ACS Symposium Series; Washington, DC, 1989; Vol. 406, pp 207−223.

(9) (a) Kazarian, S. G.; Jobling, M.; Poliakoff, M. *Mendeleev Commun.* **1993**, 148−149. (b) Cooper, A. I.; Kazarian, S. G.; Poliakoff, M. *Chem. Phys. Lett.* **1993**, *206*, 175−180. (c) Poliakoff M.; Howdle, S. M.; Kazarian, S. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1275−1295.

(10) Shim, J. J.; Johnston, K. P. *AIChE J.* **1989**, *35*, 1097−1106.

(11) (a) DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. *Science* **1994**, *265*, 356−359. (b) Clark, M. R.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 3002−3004.

(12) Adamsky, F. A.; Beckman, E. J. *Macromolecules*, **1994**, *27*, 312−314.

(13) For recent examples, see: (a) Tom, J. W.; Debenedetti, P. G. *Biotechnol. Prog.* **1991**, *7*, 403−411. (b) Mawson, S.; Johnston, K. P.; Combes, J. R.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 3182−3191. (c) Luna-Barcenas, G.; Kanakia, S. K.; Sanchez, I. C.; Johnston, K. P. *Polymer* **1995**, *36*, 3173−3182.

(14) (a) Watkins, J. J.; McCarthy, T. J. *Macromolecules* **1994**, *27*, 4845−4847. (b) Watkins, J. J.; McCarthy, T. J. *Macromolecules* **1995**, *28*, 4067−4074.

(15) Condo, P. D.; Johnston, K. P. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 523−533.

(16) Handa, Y. P.; Roovers, J.; Wang, F. *Macromolecules* **1994**, *27*, 5511−5516.

(17) Condo, P. D.; Sanchez, I. C.; Panayiotou, C. G.; Johnston, K. P. *Macromolecules* **1992**, *25*, 6119−6127.

(18) Fulton, J. L.; Yee, G. G.; Smith, R. D. *J. Am. Chem. Soc.* **1991**, *113*, 8327−8334.

(19) Yee, G. G.; Fulton, J. L.; Smith, R. D. *J. Phys. Chem.* **1992**, *96*, 6172−6181.

(20) (a) Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 9069−9079. (b) Kazarian, S. G.; Gupta, R. G.; Clarke, M. J.; Johnston, K. P.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 11099−11109.

(21) Kazarian, S. G.; Poliakoff, M. *J. Phys. Chem.* **1995**, *99*, 8624−8628.

(22) Higuchi, A.; Nakagawa, T. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 149−157.

(23) (a) Briscoe, B. J.; Kelly, C. T. *Mater. Sci. Eng.* **1993**, *A168*, 111−115. (b) Briscoe, B. J.; Kelly, C. T. *Polymer* **1995**, *36*, 3099−3102.

0002-7863/96/1518-1729$12.00/0

specific chemical CO_2−polymer interactions was reported. Although it has been suggested that CO_2 might serve as an electron donor,[26] Hildebrand et al.[27] have proposed that the solubility of CO_2 in certain aromatic solvents might arise from the ability of CO_2 to act rather as an electron acceptor. The latter is consistent with the low basicity factor for CO_2 calculated by Sigman et al.[28] In some cases there is also a possibility for weak electrostatic interactions, as has already been observed by Raman spectroscopy.[29] Reilly et al.[30] recently suggested that the interaction of liquid CO_2 with methanol might be as a Lewis acid rather than by H-bonding. Thus, one might expect similar Lewis acid−base interactions between CO_2 and other electron donor species.

Since polymers containing basic groups represent excellent electron donor candidates,[31] we have investigated a series of such polymers subjected to CO_2 by using Fourier transform infrared (FT-IR) spectroscopy. Poly(methyl methacrylate) (PMMA) is an example of a basic polymer; the electron pair on the PMMA carbonyl oxygen might interact with the carbon atom of CO_2. Such an interaction might explain the unusual swelling of PMMA[7,32] by high-pressure CO_2 or $scCO_2$. However, others have shown[22,24,25] that the antisymmetric stretching mode of CO_2 (ν_3) did not provide evidence for specific interactions between CO_2 and PMMA. Unfortunately, if CO_2−PMMA interactions are of the Lewis acid−base type, one would not expect significant changes in the CO_2 ν_3 region. Instead, one would anticipate changes in the CO_2 *bending* mode (ν_2) arising from an interaction between the carbon in CO_2 and the carbonyl oxygen of PMMA. The greater sensitivity of the ν_2 mode of CO_2 dissolved in liquids has already been demonstrated.[19,33−35] Therefore, our strategy was to use FT-IR spectroscopy to determine whether the ν_2 mode of CO_2 changed when CO_2 was incorporated into polymers containing basic functional groups. In this paper we report an IR spectroscopic study of CO_2 dissolved in several polymer systems.

Experimental Section

We used FT-IR transmission and ATR (attenuated total reflection)-IR spectroscopy. For the transmission FT-IR work, we constructed a special high-pressure optical cell, similar to previous designs,[9c,36] equipped with ZnSe windows that allowed us to observe the ν_2 spectral region (680−600 cm^{-1}). We used a commercial ATR-IR high-pressure cell from Spectra Tech (CIRCLE) with a ZnSe crystal. It was also important to choose polymers which do not absorb strongly in the region of the CO_2 ν_2 mode. Fortunately, PMMA and all the other polymers studied here exhibited little if any absorption in the spectral region of interest.

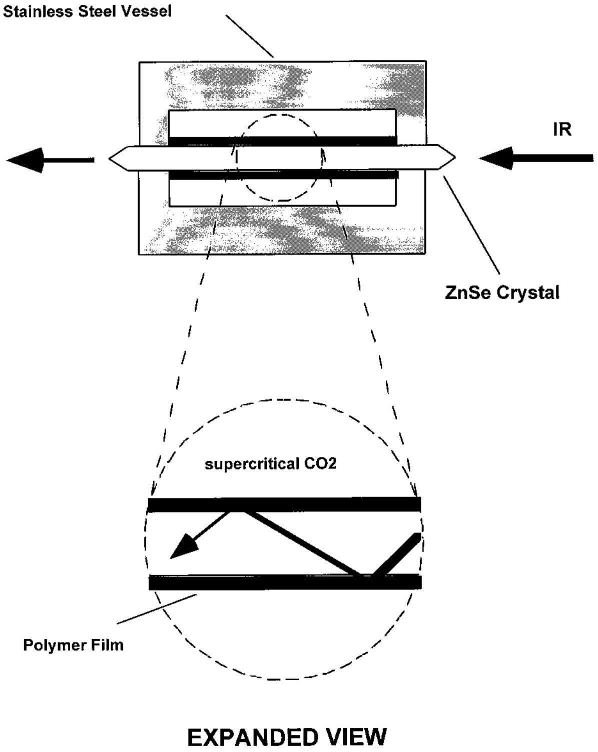


Figure 1. Schematic view of ATR-IR cell. High-pressure sealings on the ZnSe crystal are Teflon O-rings. The cell was pressurized with CO_2 via the high-pressure pump (Isco, Inc., Model 100 DX) with 1/16 in. o.d. stainless steel tubing. The increased scale shows the polymer film cast on the ATR crystal.

Polymer films were prepared by casting from CH_2Cl_2 or by hot-pressing. Films for study were then placed into the IR high-pressure cell, and CO_2 was introduced directly using a syringe pump at room temperature. The experiments at constant temperature were done in the range 25−40 °C. Our IR transmission cell is able to withstand pressures in excess of 170 bars, but the CO_2 absorbance becomes too high even around P_c (74 bars). This is due to the relatively long path length of the cell (which was adjustable between 2 and 4 mm). ATR-IR spectroscopy gives path lengths of several micrometers depending on the number of reflections, refractive indices, and incidence angle.[37] ATR spectroscopy has already been used under high pressures[38] and very recently for the study of supercritical fluids.[39] The use of ATR-IR is a well-known approach for studying polymer films.[40]

To minimize the absorbance from bulk CO_2, we cast polymer films from CH_2Cl_2 onto the ATR crystal (Figure 1). The use of ATR-IR spectroscopy also helps to eliminate any possible artifacts resulting from CO_2 molecules adsorbed on the polymer surface. The high-pressure ATR cell was able to withstand pressures up to 100 bars. FT-IR spectra were measured on a Nicolet 520 spectrometer with DTGS detector; resolution was 1−2 cm^{-1}.

PMMA and poly(2-vinylpyridine) (P2VP) were purchased from Polysciences, Inc., poly(vinyl acetate) (PVAc), poly(ethylene terephthalate) (PET), poly(vinyl methyl ketone) (PVMK), low-density poly(ethylene) (PE), poly(butyl methacrylate) (PBMA), poly(ethyl methacrylate) (PEMA), and the copolymers of poly(ethylene−vinyl acetate) were purchased from Aldrich Chemical Co. Poly(vinyl fluoride) (PVF) was supplied by DuPont and poly(styrene) (PS) by 3M. High-purity carbon dioxide, 99.99% was supplied by Matheson.

---

(24) Fried, J. R.; Li, W. J. *Appl. Polym. Sci.* **1990**, *41*, 1123−1131.

(25) Pyrkov, A. V.; Makarova, N. I.; Blednykh, E. I. *Polym. Sci., Ser. B* *36*, **1994**, 1005−1006.

(26) Hyatt, J. A. *J. Org. Chem.* **1984**, *49*, 5097−5101.

(27) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand Reinhold Co.: New York, 1970.

(28) Sigman, M. E.; Lindley, S. M.; Leffler, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 1471−1472.

(29) Zerda, T. W.; Song, X.; Jonas, J. *Appl. Spectrosc.* **1986**, *40*, 1194−1199.

(30) Reilly, J. T.; Bokis, C. P.; Donohue, M. D. *Int. J. Thermophys.* **1995**, *16*, 599−610.

(31) Fowkes, F. M.; Tischler, D. O.; Wolfe, J. A.; Lannigan, L. A.; Ademu-John, C. M.; Halliwell, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **1984**, *22*, 547−566.

(32) Blednykh, E. I.; Skripov, V. P. *Vysokomol. Soedin., Ser. B* **1992**, *34*, 61−65.

(33) Cunliffe-Jones, D. B. *Spectrochim. Acta* **1969**, *25A*, 779−791.

(34) Heald, C.; Thompson, H. W. *Proc. R. Soc.* **1962**, *A268*, 89−99.

(35) Dobrowolski, J. C.; Jamroz, M. H. *J. Mol. Struct.* **1992**, *275*, 211−219.

(36) Lokshin, B. V.; Kazarian, S. G.; Ginzburg, A. G. *J. Mol. Struct.* **1988**, *174*, 29−34.

(37) Harrick, N. J. *Internal Reflection Spectroscopy*; Harrick Scientific Corp.: Ossining, NY, 1987.

(38) Moser, W. R.; Cnossen, J. E.; Wang, A. W.; Krouse, S. A. *J. Catal.* **1985**, *95*, 21−32.

(39) Yokoyama, C.; Kanno, Y.; Takahashi, M.; Ohtake, K.; Takahashi, S. *Rev. Sci. Instrum.* **1993**, *64*, 1369−1370.

(40) (a) See, for example: Gobel, R.; Seitz, R. W.; Tomellini, S. A.; Krska, R.; Kellner, R. *Vib. Spectrosc.* **1995**, *8*, 141−150. (b) Sutandar, P.; Ahn, D. J.; Franses, E. I. *Macromolecules* **1994**, *27*, 7316−7328. (c) Van Alsten, J. G.; Lustig, S. R. *Macromolecules* **1992**, *25*, 5069−5073.

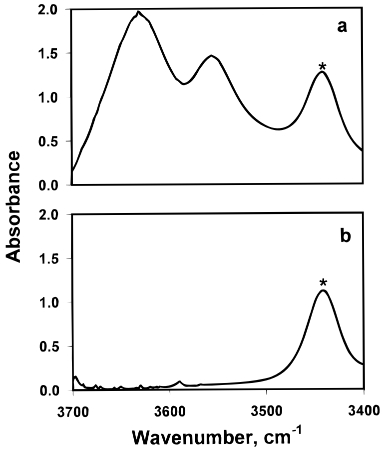


Figure 2. IR absorption spectra of PMMA film covering the ν(O−H) region showing the effect of $scCO_2$ drying of the polymer film at 40 °C. The overtone, 2ν(C−O), of PMMA also absorbs in this region, the corresponding band marked with an asterisk: (a) spectrum of the PMMA film *before* applying $scCO_2$ and (b) spectrum of the same film *after* the cell was flushed with $scCO_2$ for 2 h.

Many polymers can adsorb significant quantities of water;[41] PMMA is one of the best studied examples.[40b] Therefore special attention has been paid to the removal of water from the polymer films. Vacuum and heating may take several hours to dry polymer films. A more rapid approach was drying the films with $scCO_2$.[42] Figure 2 shows the IR spectrum of PMMA before and after applying $scCO_2$ to the film. The bands at 3630 and 3550 cm^{-1} are asymmetric and symmetric stretching vibrations of the water molecules weakly bonded to PMMA.[40b,43] The absorption bands due to the presence of the water in the virgin PMMA film have disappeared after $scCO_2$ processing. The decrease in band intensities was also accompanied by the disappearance of the band at 1630 cm^{-1} assigned to the bending mode of water (not illustrated). We observed similar results for the other polymers studied. We were also able to investigate $scCO_2$ drying *in situ* by using D_2O, which allowed us to separate otherwise overlapping bands of water from the combination bands of CO_2. H_2O can interact with CO_2;[44,45] therefore trace amounts of water were removed from our polymer films prior to study.[46]

Results and Discussion

PMMA and CO_2. We begin with the results from the transmission IR spectroscopy of the polymer system. As mentioned above, the strong absorption of bulk CO_2 surrounding the polymer film prevents direct observation of the spectrum of CO_2 incorporated into the polymer. However, if the polymer film is subjected to CO_2 (41−83 bars) for a period of about 1 h, and the pressure is then slowly released,[47] one can observe directly the behavior of CO_2 molecules sequestered within the polymer film.

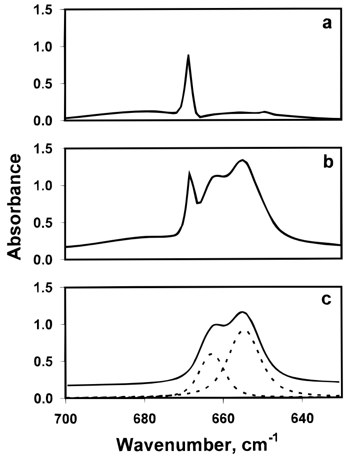
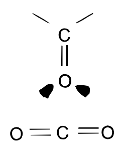


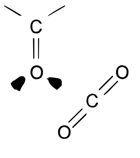
Figure 3. IR absorption spectra of CO_2 in the ν_2 bending mode region: (a) gaseous sample, (b) PMMA film impregnated with CO_2 immediately after decompression, and (c) film after removal of gaseous CO_2. The dashed lines are the curve fit spectrum (peak fit) of Figure 3c ($r^2 = 0.9998$).

Figure 3 presents IR absorption spectra of CO_2 vapor in the absence of a polymer film (a) and CO_2 entrapped within PMMA films (b and c). The central and lower traces show spectra acquired immediately following depressurization and application of vacuum on the film, respectively. Three main bands (667, 662, and 654 cm^{-1}) are evident in the freshly depressurized PMMA−CO_2 film (Figure 3b). In contrast, the 667 cm^{-1} band is not present in the "evacuated" film (Figure 3c), but the bands at 662 and 654 cm^{-1} remain. This is consistent with the 667 cm^{-1} band arising from free, unassociated CO_2, presumably due to gaseous CO_2 surrounding the PMMA film within the cell (Figure 3a). The new absorption bands at 662 and 654 cm^{-1} appear as peaks on the broad band shifted to lower frequency from the gaseous CO_2 Q-branch. We were able to resolve successfully this shifted band envelope into two discrete bands (Figure 3c).

These new bands have been assigned to the ν_2 mode of CO_2 interacting with the carbonyl of PMMA. If this type of Lewis acid-base interaction takes on a T-shaped geometry (structure a) or a "bent" T-shape configuration (structure b), the degeneracy of the ν_2 mode will be released. Thus the $D_{\infty h}$ symmetry inherent in free CO_2 will no longer exist for carbonyl-associated CO_2, and an overall C_{2v} or C_s symmetry will result. In this case two absorption bands will appear (Figure 3c) from out-of-plane and in-plane bending modes. The larger shift will be associated with the in-plane mode (654 cm^{-1}), where the plane in the T-shaped type complex is defined by the lone pair of the oxygen atom of the carbonyl group of the polymer and O=C=O



a



b

---

[41] Rowland, S. P. Water in Polymers. *ACS Symp. Ser.* 1980, *127*.

[42] $scCO_2$ has already been used for drying; see, for example: (a) Novak, B. M.; Auerbach, D.; Verrier, C. *Chem. Mater.* **1994**, *6*, 282−286. (b) van Bommel, M. J.; de Haan, A. B. *J. Mater. Sci.* **1994**, *29*, 943−948.

[43] (a) Pakhomov, P. M.; Kropotova, E. O.; Zubkov, A. I.; Levin, V. M.; Chegolya, A. S. *Polym. Sci.* **1992**, *34*, 1001−1004. (b) Pakhomov, P. M.; Khizhnyak, S. D.; Belyakova, T. I. *Polym. Sci., Ser. A* **1995**, *37*, 164−169. (c) Gilbert, A. S.; Pethrick, R. A.; Phillips, D. W. *J. Appl. Polym. Sci.* **1977**, *21*, 319−330. (d) Avakian, P.; Hsu, W. Y.; Meakin, P.; Snyder, H. L. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1607−1613. (e) Kusanagi, H.; Yukawa, S. *Polymer* **1994**, *35*, 5637−5640.

[44] (a) Fredin, L.; Nelander, B.; Ribbegard, G. *Chem. Scrip.* **1975**, *7*, 11−13. (b) It has also been shown that the hydrogen-bonded water with some basic sites might result in enhanced basicity of the oxygen atom of the water thus increasing its reactivity toward the CO_2 carbon atom: Quinn, R.; Appleby, J. B.; Pez, G. P. *J. Am. Chem. Soc.* **1995**, *117*, 329−335.

[45] (a) Peterson, K. I.; Klemperer, W. *J. Chem. Phys.* **1984**, *80*, 2439−2445. (b) Nguyen, M. T.; Ha, T. K. *J. Am. Chem. Soc.* **1984**, *106*, 599−602. (c) Block, P. A.; Marshall, M. D.; Pedersen, L. G.; Miller, R. E. *J. Chem. Phys.* **1992**, *96*, 7321−7332. (d) Cox, A. J.; Ford, T. A.; Glasser, L. *J. Mol. Struct.* **1994**, *312*, 101−108.

[46] It was also important to remove any possible impurities from the polymer films. Residual monomer or low molecular weight oligomers of PMMA were extracted using $scCO_2$ with concomitant detection in a specially designed IR cell: Kazarian, S. G.; Vincent, M. F.; Eckert, C. A. *Rev. Sci. Instrum.*, in press.

[47] The quick release of the pressure of CO_2 can cause foaming of the polymer film[7,25,32] with the formation of numerous bubbles within the film, thus making the film essentially opaque for IR studies. The foaming is more likely when the pressure is released at higher temperatures.[32]

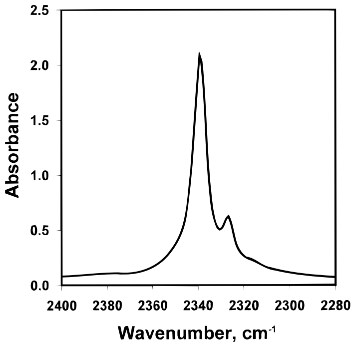


Figure 4. IR absorption spectrum of CO_2 impregnated into PMMA film in the ν_3 antisymmetric stretching mode region.

axis. A larger shift for the in-plane mode and the relative intensities of this doublet are in agreement with the changes predicted by *ab initio* calculations for the bending mode of CO_2 acting as *an electron acceptor* in the $(CO_2)_2$ dimer.[48c] From the experimental evidence we cannot discern the exact geometry of the complex; however, the splitting of the bending mode of CO_2 with almost unaffected stretching mode of CO_2 in PMMA (see below) strongly supports the configuration of the complex in which the carbon atom of CO_2 molecule acts as an electron acceptor. This could take place when the carbon atom of the CO_2 molecule interacts with the lone pair of electrons on the carbonyl oxygen as in structure b above. One might contend that because of steric hindrance the CO_2 axis could be 90° out of the plane of the paper (C_1 symmetry). Regardless of the angle of rotation in structure b, the nature of the interaction is primarily Lewis acid−base. There are, however, *ab initio* calculations[45a,c,48c,49] which indicate that the CO_2 molecule might have a T-shaped configuration (structure a) interacting with both electron lone pairs.

The splitting of the ν_2 mode of PMMA-entrapped CO_2 provides strong evidence for specific chemical interactions between CO_2 and PMMA. The fact that Figure 3c shows only a split doublet for ν_2 indicates that all CO_2 molecules remaining in the polymer film (i.e., approximately infinite dilution condition) are complexed and interact with the carbonyl groups of PMMA.

Spectral changes in the ν_3 antisymmetric stretching region also support the above conclusion; only a band at 2338 cm^{-1} and a weak low-frequency band at 2326 cm^{-1} (assigned to the $(\nu_3 + \nu_2) - \nu_2$ hot-band)[33] are observed (Figure 4). The fact that only one band corresponding to the CO_2 ν_3 mode appears in the spectrum suggests that there is only one type of the site within the polymer matrix for CO_2 molecules under these conditions. If there were two or more inequivalent sites for the CO_2 molecules within the polymer matrix, one would expect more than one band in the ν_3 region. Temperature-dependent studies show that an increase in temperature leads to a simultaneous decrease of the intensities of the bands at 2338, 662 and 654 cm^{-1} (with a concomitant growth in the gaseous CO_2 bands in the cell). Importantly, within the temperature range (20−60 °C), the ratio of the intensities of these two bands in the doublet remain the same. This eliminates any suggestion of two inequivalent CO_2 sites within the PMMA film, since in that case one would expect that the band corresponding to the more weakly interacting CO_2 would decrease first. We suggest that the results of the other workers,[25] where the complex structure of ν_3 mode of CO_2 dissolved in PMMA was observed, may be due to the presence of the residues of the solvent used to cast the PMMA film.

We estimated the extinction coefficient of the ν_2 absorption band of CO_2 bound to PMMA by observing the degassing of the polymer film in a closed IR transmission cell. Since total mass is conserved, we write:

$$V_p \Delta c_p = -V_g \Delta c_g \tag{1}$$

where Δc_p and Δc_g are the changes in CO_2 concentrations in the polymer film and in the gas phase, respectively, and V_p and V_g are the volumes of the polymer film and the cell, respectively. At the same time we can measure c_p and c_g spectroscopically (assuming that CO_2 is distributed uniformly in the film) using the Lambert−Beer law:

$$c_g = \frac{A_g}{\epsilon_g L_g}$$

where the A_g is absorbance of the gas, ϵ_g is the extinction coeffecient, and L_g is the optical path length for gaseous CO_2 in the cell;

$$c_p = \frac{A_p}{\epsilon_p L_p}$$

Applying c_g and c_p from these equations into (1),

$$\frac{\epsilon_g}{\epsilon_p} = \frac{-\Delta A_g V_g L_p}{\Delta A_p V_p L_g} \tag{2}$$

We found that that extinction coefficient of the band corresponding to the ν_2 mode of the CO_2 interacting with the polymer is severalfold higher than the value for free gaseous CO_2. Such an increase in extinction coefficient is probably due to the small charge transfer from the carbonyl group to CO_2 and is typical for the donor−acceptor interactions.

We did not detect new bands in the 1600−1300 cm^{-1} region where one might expect a ν_1 mode for bent CO_2 molecules. This suggests that the polymer-associated CO_2 molecules retain their linear structure. However, we cannot exclude a small degree of CO_2 bending leading to a weak new band that might be masked by the stronger PMMA absorption bands. Moreover, the intensity of the symmetric stretching mode in weak CO_2 complexes is also thought to be very weak.[48a−c] Recent work by Jamroz et al.[49] on *ab initio* calculation of the Lewis acid−base interaction of CO_2 shows that the angle of bending of CO_2 molecules in such complexes will be only a few degrees.

The ν_2 mode splitting is the only spectroscopic evidence for a specific CO_2−PMMA interaction, but additional support for our characterization of the interaction as being of a Lewis acid−base nature with the T-shape type structure stems from the *ab initio* and experimental studies of different weak CO_2 complexes;[48,49] however, as the CO_2 molecule has a substantial quadrupole moment, we cannot entirely exclude the contribution of electrostatic forces in the interaction of CO_2 with PMMA.

We observed identical results with those in Figure 3 for both hot-pressed and solution cast PMMA films. In order to exclude the possibility that the ν_2 splitting is a result of the pretreatment of the PMMA samples, we applied photoacoustic spectroscopy

---

(48) (a) Fredin, L.; Nelander, B. *Chem. Phys.* **1976**, *15*, 473. (b) Nxumalo, L. M.; Ford, T. A. *J. Mol. Struct.* **1994**, *327*, 145−159. (c) Nxumalo, L. M.; Ford, T. A.; Cox, A. J. THEOCHEM **1994**, *307*, 153−169. (d) Novick, S. E.; Davies, P. B.; Dyke, T. R.; Klemperer, W. *J. Am. Chem. Soc.* **1973**, *95*, 8547−8550. (e) Bone, R. G. A.; Handy, N. C. *Theor. Chim. Acta* **1990**, *78*, 133. (f) Recent, but slightly less relevant, examples to our results of IR spectroscopy and *ab initio* calculations on CO_2 clusters include: Knozinger, E.; Beichert, P. *J. Phys. Chem.* **1995**, *99*, 4906−4911. Ovchinnikov, M.; Wight, C. A. *J. Chem. Phys.* **1994**, *100*, 972−877. Disselkamp, R.; Ewing, G. E. *J. Chem. Phys.* **1993**, *99*, 2439−2448.

(49) Jamroz, M. H., Dobrowolski, J. C.; Bajdor, K.; Borowiak, M. A. *J. Mol. Struct.* **1995**, *349*, 9−12.

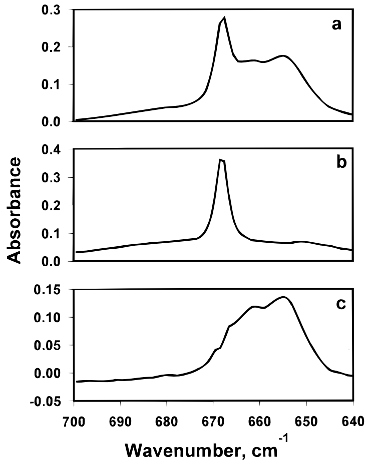


Figure 5. ATR-IR spectra of CO_2 in the ν_2 mode region at 40 °C: (a) PMMA film subjected to 27.5 bar of CO_2, (b) spectrum of gaseous CO_2 at 27.5 bar in ATR-IR cell *without* PMMA film, and (c) result of subtraction of spectrum b from spectrum a.

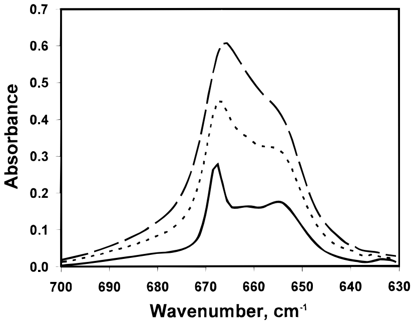


Figure 6. ATR-IR spectra of PMMA film subjected to high-pressure CO_2 in the ν_2 mode region at 35 °C. CO_2 pressure is 27.5 bar (solid line), 55.2 bar (dotted line), and 89.7 bar (dashed line).

to the PMMA pellets as received from the supplier (with preliminary vacuum drying).[50] The spectrum in the region of the bending mode of CO_2 incorporated into these pellets (not shown) is almost the same as the transmission spectrum of the film, confirming that the observed splitting is not the result of the film preparation scheme.

In our transmission FT-IR experiments, we were unable to observe *in situ* how CO_2 penetrates into polymer films because of the strong absorption from the bulk CO_2 surrounding the polymer film. Fortunately, ATR-IR spectroscopy allows one to observe liquid penetration into polymer films *in situ* and to measure the sorption kinetics of the solutes in the polymer matrices.[40,51] The spectra in Figure 5 show that the ATR-IR spectrum of a PMMA film subjected to 27.5 bars of CO_2 has the same doublet band structure as observed in the transmission experiments (Figure 3), indicating interaction between CO_2 and the PMMA film. In these experiments we were able to observe the spectrum of dissolved CO_2 in PMMA up to 100 bars.

Figure 6 shows the effect of pressure on the spectrum in the bending mode region of CO_2. At 27.5 bars, the dominant feature is a doublet representing CO_2 that is weakly bonded to the carbonyl groups in PMMA. At higher pressures the spectrum shows a single band (although with a shoulder on the low-frequency side). These spectral changes can be rationalized as follows. (i) Increasing CO_2 pressure causes a concomitant increase of CO_2 concentration within the PMMA film. The CO_2 dissolved within the polymer film interacts weakly with the available carbonyl groups of PMMA. Perhaps the initial interaction of CO_2 molecules with CO groups of the polymer may be responsible for the preliminary swelling of PMMA, which in turn may assist further "partitioning" of additional CO_2 molecules into PMMA. (ii) As the pressure increases, CO_2 continues to partition into PMMA. CO_2 "partitioning" leads to the appearance of the single absorption band due to dissolved, noninteracting CO_2 molecules in PMMA. (iii) The absorption from polymer-sequestered (but not specifically interacting) CO_2 molecules dominates the spectrum at high CO_2 pressures and apparently obscures the doublet band associated with interacting CO_2 molecules. (iv) Also, the glass transition temperature (T_g) of PMMA decreases[4b,7,52] to near room temperature when the polymer is subjected to high-pressure CO_2; thus, the rigidity of the polymer chains is decreased. Therefore, the increased mobility of CO_2 molecules dissolved in the polymer and the apparent dissapearance of a hindrance for internal rotation presumably make the alignment of the CO_2 molecule toward the carbonyl oxygen more difficult. This results in the absence of the splitting of the bending mode of CO_2. All spectral changes demonstrated in Figure 6 were reproducible with increasing or decreasing CO_2 pressures.

To determine how the PMMA spectrum itself is affected by CO_2, we viewed it carefully before and after applying CO_2. We did not see a lowering of the band frequency at 1731cm^{-1}, which corresponds to C═O vibration of the carbonyl group of PMMA. A decrease in the frequency of this band has been observed when PMMA was subjected to the proton donors, apparently due to H-bonding. By contrast, a small frequency increase (ca. 2 cm^{-1}) of the carbonyl band was observed when the PMMA film was subjected to high-pressure CO_2. A similar result obtained by others has been compared[24] with the literature data on the carbonyl bands of PMMA interacting with the different Lewis acids. Actually such a comparison is not valid because these interactions cause the low-frequency shifts of the carbonyl band. In that work the interaction between CO_2 and the carbonyl group of PMMA was assigned to weak dipole−dipole interaction. We, however, observed similar small high-frequency shifts for other bands of PMMA while subjected to high-pressure CO_2; therefore, we suggest that these small changes in the PMMA spectrum itself indicate changes in the local dielectric constant of the PMMA carbonyl groups from dissolved CO_2.

The spectral shifts of IR bands cannot be explained solely by the changes in the dielectric field[33,53] if specific intermolecular interactions occur simultaneously. However, these factors cause the ν(C═O) band to shift in opposite directions. Thus, it is likely that the high-frequency shift of the ν(C═O) band of PMMA when subjected to CO_2 is due to the compensating effect of the changes in the dielectric environment of carbonyl groups of PMMA. Indeed, it has been shown that toluene should cause a 6 cm^{-1} high-frequency shift,[31] while at the same time other work suggested that CO_2 exhibits a similar solvent effect on vibrational frequencies to that of toluene.[26] In this scenario a much smaller shift (ca. 2 cm^{-1}) in the case of CO_2 might be explained by specific interactions, which almost totally compensate for the changes in the dielectric field.

These results indicate that the strength of the specific interaction of the carbonyl group of PMMA (electron donor) with CO_2 (electron acceptor) is very weak. No exact measure is evident from our data, but rough estimates can be postulated.

---

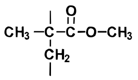
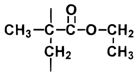
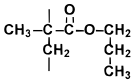
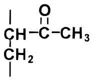
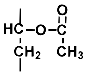
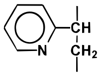
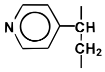
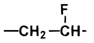
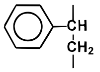
(50) We are very grateful to Dr. J. F. McClelland (MTEC Photoacoustics, Inc.) for the measurements of FT-IR photoacoustic spectra.

(51) (a) Fieldson, G. T.; Barbari, T. A. *Polymer* **1993**, *34*, 1146−1153. (b) Pereira, M. R.; Yarwood, J. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 1881−1887. (c) Farinas, K. C.; Doh, L.; Venkatraman, S.; Potts, R. O. *Macromolecules* **1994**, *27*, 5220−5222.

(52) Condo, P. D.; Johnston, K. P. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 523−533.

(53) Iogansen, A. V.; Rassadin, B. V.; Romancova, G. E.; Grushina, N. M. *Opt. Spectrosc.* **1978**, *44*, 1104−1112.

Table 1. Wavenumbers of ν_2 and ν_3 Modes of CO_2 in Polymer Films[a]

Polymer		ν_2, Wavenumber (cm^{-1})		ν_3, Wavenumber (cm^{-1})
PMMA	 $CH_3-\underset{\underset{\vert}{CH_2}}{\overset{\vert}{C}}-\overset{O}{\overset{\Vert}{C}}-O-CH_3$	662.6	654.6	2338.0
PEMA	 $CH_3-\underset{\underset{\vert}{CH_2}}{\overset{\vert}{C}}-\overset{O}{\overset{\Vert}{C}}-O-\underset{CH_3}{\underset{\vert}{CH_2}}$	663.0	654.7	2338.8
PBMA	 $CH_3-\underset{\underset{\vert}{CH_2}}{\overset{\vert}{C}}-\overset{O}{\overset{\Vert}{C}}-O-\underset{\underset{CH_3}{\underset{\vert}{CH_2}}}{\underset{\vert}{CH_2}}$	662.1	654.4	2338.0
PVMK	 $\underset{\underset{\vert}{CH_2}}{\overset{\vert}{C}H}-\overset{O}{\overset{\Vert}{C}}-CH_3$	661.7	652.6	2339.0
PVAc	 $\underset{\underset{\vert}{CH_2}}{\overset{\vert}{HC}}-O-\underset{\underset{CH_3}{\vert}}{\overset{O}{\overset{\Vert}{C}}}$	661.9	654.0	2339.5
PV2P		658 (asymmetric)[b]		2335.3
PV4P		658 (asymmetric)[c]		2334.6
PVF	 $-CH_2-\overset{F}{\overset{\vert}{C}H}-$	662.5	657.8	2340.6
PE	$-CH_2-CH_2-$	659.0		2335.0
PS		657.2		2334.9

[a] Error ± 0.2 cm^{-1}. [b] Band is broad and has asymmetric shape (see Figure 7). The wavenumber of peak maximum is given. Peak fit of the band shows three bands under the envelope: 660.1, 646.5, and 653.7 cm^{-1}. [c] The wavenumber of peak maximum is given. Peak fit of the asymmetric band shows three bands under the envelope: 659.8, 653.6, and 642.8 cm^{-1}.

Since the $\nu(C{=}O)$ frequency of PMMA saturated by CO_2 is 1733 cm^{-1}, the $\Delta\nu(C{=}O)$ is 4 cm^{-1} compared to toluene solutions. We estimate the energy from[31]

$$\Delta H = 0.236\Delta\nu(C{=}O)$$

where ΔH is in kcal/mol and $\Delta\nu$ is in cm^{-1}. This yields an enthalpy for the acid−base interaction of CO_2 with the PMMA carbonyl group of ca. 1 kcal/mol, comparable to the energy of London forces.

One must consider several spectral bands in order to understand the nature of CO_2−polymer interactions. By contrast, previous IR studies on CO_2−PMMA considered only the $\nu(C{=}O)$ band of PMMA[24] or measured the ν_3 antisymmetric stretch of CO_2.[22,25] Surprisingly, the most sensitive band of CO_2, ν_2, has not been considered in any of the previous reports on polymers. Using the same concepts described for the PMMA−CO_2 interaction, we now describe the interactions between CO_2 and other polymers.

Interaction of CO_2 with Other Polymers. The intermolecular interaction of CO_2 with PMMA suggested that this type of interaction might occur between CO_2 and other polymers containing Lewis base groups. Table 1 shows new, split ν_2 bands shifted to lower energy for CO_2 interacting with polymers possessing basic groups.

PEMA and PBMA. Specific interactions were also detected for CO_2 with PEMA and PBMA. The shift and the splitting of the ν_2 bending mode of CO_2 sequestered within these two polymers are almost identical with those seen for PMMA films. However, these particular polymer analogs have quite different glass transition temperatures (63 and 27 °C, respectively). Thus, the PBMA was above T_g (at low CO_2 pressures), but the spectra of the incorporated CO_2 were similar to those in PMMA and PEMA films. However, the desorption of CO_2 from the PBMA film upon pressure release was much faster. The PBMA is above its T_g under our conditions, which led to significantly reduced rigidity of the polymer chains and thus faster desorption of CO_2.

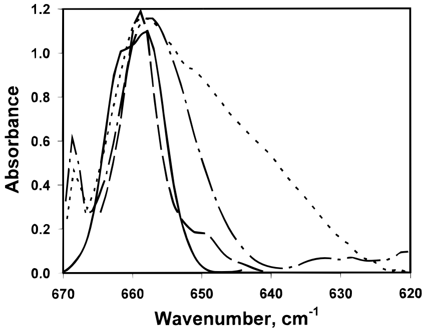


Figure 7. IR spectra of CO_2 in the ν_2 mode region: spectrum of PE film impregnated with CO_2 (dashed line), spectrum of PS film impregnated with CO_2 (dashed−dotted line), spectrum of PVF film impregnated with CO_2 (solid line), and spectrum of PV2P film impregnated with CO_2 (dotted line). The absorbance scale of these superimposed spectra have been normalized to the absorbance of the stronger band.

PVMK. The degree of splitting of the ν_2 bending mode of CO_2 incorporated into PVMK film is nearly the same as in PMMA. The low-frequency shift of this doublet in comparison with the ν_2 mode of free gaseous CO_2 was also similar and just somewhat larger (Table 1). Thus, our suggestion that CO_2 interacts with the oxygen atom of the carbonyl group in PMMA is supported by this experiment because there is no ester oxygen atom in PVMK.

PVAc and Nylon 6. The splitting of the CO_2 ν_2 mode was also observed in the case of PVAc (Table 1) and nylon 6. In the latter case, the amount of specific polymer−CO_2 species detected within the polymer film is rather small. This may result from inter- and intrapolymer interactions between carbonyl and amide groups (i.e., H-bonding) that lead to a situation where neither of the basic sites in the polymer is readily available for the specific interactions with CO_2. This suggestion is supported by the absence of the CO_2 ν_2 splitting in PMMA films that are impregnated by methanol. Apparently, H-bonding of methanol blocks the carbonyl groups, making them unavailable for the interaction with CO_2. The fact that we did detect small amounts of bound CO_2 in nylon 6 provides plausible rationalization of the work of Briscoe et al.,[23] where the authors observed a small disruption of the hydrogen bonding within the polymer by looking at the $\nu(N-H)$ absorption bands of poly(urethane) elastomers subjected to high-pressure CO_2.

PE and PS. No v_2 band splitting was observed for CO_2 with PE[53] or PS polymer films (Figure 7). These polymers do not posses strong Lewis base sites like the carbonyl oxygen atoms. The bandwidth of ν_2 band of CO_2 in poly(styrene) was broader than in the case of poly(ethylene) (12 vs 8 cm^{-1}). This indicates some distortion of the bending mode consistent with weak electrostatic interactions of CO_2 with the π-system (phenyl ring) in PS. This is supported by the results of CNDO/2 calculations for complexes of CO_2 with benzene, which have been assigned to electrostatic interactions.[55]

---

(54) IR spectra of CO_2 within poly(ethylene) film have been reported for ν_3 mode: (a) Webb, J. A.; Bower, D. I.; Ward, I. M.; Cardew, P. T. *Polymer* **1992**, *33*, 1321−1322. For both ν_3 and ν_2 modes: (b) Radziszewski, J. G.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 3289−3297.

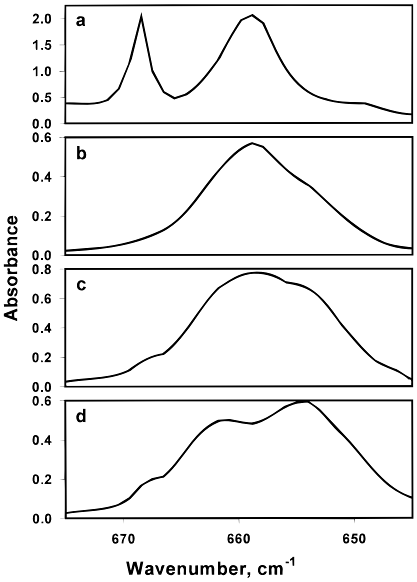


Figure 8. IR spectra of CO_2 in the ν_2 mode region in the films impregnated by CO_2: (a) PE film impregnated by CO_2, (b) film of copolymer poly(ethylene−vinyl acetate) (14 wt %), (c) film of copolymer poly(ethylene−vinyl acetate) (33 wt %), and (d) film of PVAc.

Copolymers: Poly(ethylene−vinyl acetate). In order to verify that the splitting of the v_2 mode is due solely to the interaction with the basic sites in polymers, we studied a copolymer of poly(ethylene−vinyl acetate) containing varying numbers of basic sites. In the PE film the ν_2 mode of incorporated CO_2 is not split (Figure 7), while in the PVAc film distinct splitting was observed (Table 1). In a copolymer containing 14% vinyl acetate, slight broading of the ν_2 band of incorporated CO_2 is observed. This result is understandable if CO_2 was simultaneously incorporated into the domains containing vinyl acetate groups and poly(ethylene) domains. When a copolymer containing 33% vinyl acetate was used, the broadening became more pronounced (Figure 8). This broadening indicates that there are additional bands under the broad ν_2 envelope of CO_2 incorporated in this copolymer. The distortion of the ν_2 band is indeed due to the presence of the basic sites within the polymer samples. These data concur with the observation of Berens et al.,[8] who observed a steady increase in CO_2 sorption in such copolymers with increasing vinyl acetate content and also proposed that specific interactions might be responsible for this effect. Our data also explain the results of Koros,[2d] who found that the CO_2 solubility increased with the density of carbonyl groups in the polymer and also suggested that the results might be due to specific intermolecular interactions between CO_2 and the carbonyl groups. Our spectroscopic results are the first evidence of specific interaction of CO_2 with polymers and might be useful in discussions of the dual-mode sorption model.[2]

PV2P and PV4P. The ν_2 mode of CO_2 incorporated into PV2P or PV4P films is much broader (ca. 24 cm^{-1}), even more than the CO_2 ν_2 band in PS (Figure 7), indicating that the basic nitrogen atom in these polymers interacts with CO_2. However, no distinct splitting of ν_2 is observed for CO_2 within these films. Apparently the contributions of both Lewis acid−base interactions (with the nitrogen atom) and electrostatic interactions (with the π-system of the ring) preclude such a discrete band observation. Weak acid−base interaction between CO_2 and the polymer moiety containing the basic nitrogen atom has been proposed in other relevant polymer systems.[56]

PET. Poly(ethylene terephthalate) provides another example where at least two functional groups may interact with CO_2—the phenyl ring and the carbonyl group.[2b] The band of the ν_2 mode of CO_2 in PET film was indeed distorted; the doublet at 659 and 655 cm^{-1} was observed. This observation indicates some specific interaction of CO_2 with this polymer. The splitting of the band was somewhat smaller than the splitting observed in other carbonyl-containing polymers (e.g., PMMA or PVMK). The presence of the several basic sites in PET together with its comprehensive microstructure and morphology[2b] makes assignment of the observed splitting a complicated task. Further experiments will be needed to resolve this point.

PVF. The fluorine atoms in PVF constitute weak basic sites. Figure 7 shows the difference in ν_2 modes of CO_2 incorporated into PE and PVF films. In the latter case, only minor splitting (ca. 4 cm^{-1}) is observed. We assign this result to weak electrostatic interaction of CO_2 with the C−F dipole in PVF. Very similar ν_2 band splitting of CO_2 (661 and 658 cm^{-1}) was observed for carbon dioxide clathrate hydrate at low temperature.[57] However, different sites within the matrix cage were used to explain the splitting.

Additional Considerations. Splitting of the ν_2 mode was observed in other low-temperature studies,[58] due to the removal of degeneracy of the ν_2 mode in the crystalline solid CO_2. The bending ν_2 mode is a more sensitive structural probe, but these authors did not use this probe when they studied the possibility of H-bonding between water and carbon dioxide.[59] They did not find H-bonding and assigned the interaction of carbon dioxide with the oxygen atom of water. Similar interactions have also been proposed to explain the large change in intensity of the band of the antisymmetric stretching mode ν_3 of CO_2 dissolved in supercritical water.[60] These findings are consistent with the proposed Lewis acid−base interactions in our work on CO_2 with oxygen-containing polymers.

Thus the ν_2 bending mode of CO_2 is an excellent probe of the weak interactions in different media as diverse as membranes[2] and biological fluids.[61] The higher sensitivity of the ν_2 mode of CO_2 incorporated into polymer films in comparison to the ν_3 mode is shown in the Table 1. In all cases the ν_3 absorption of CO_2 is within a very narrow frequency range (2340−2335 cm^{-1}). These results are consistent with the proposed T-shaped type of structure for the interaction of CO_2 with the basic sites in the polymers.

Although we were not able to determine the energy of the specific interaction of CO_2 with every polymer studied, we discovered that the width of the ν_2 absorption band of CO_2 impregnated into polymers might be used to estimate the strength of such interaction. Table 2 demonstrates a difference in the widths of the ν_2 band of CO_2 dissolved in several polymers. The specific interaction with functional groups in the polymers leads to the distortion of the band of ν_2 mode of CO_2, and this band splits; the interaction is assigned to Lewis acid−base interactions. Assuming that CO_2−polymer interactions are responsible for the solubility of CO_2 in the polymers, the width of ν_2 band should correlate with the measured solubility of CO_2 in polymers. Solubility data from the literature

---

(55) Nandel, F. S.; Jain, D. V. S. *Indian J. Chem.* **1984**, *23A*, 543−545.

(56) (a) Yoshikawa, M.; Ezaki, T.; Sanui, K.; Ogata, N. *J. Appl. Polym. Sci.* **1988**, *35*, 145−154. (b) Rebattet, L.; Escoubes, M.; Genies, E.; Pineri, M. *J. Appl. Polym. Sci.* **1995**, *58*, 923−933.

(57) Fleyfel, F.; Devlin, J. P. *J. Phys. Chem.* **1991**, *95*, 3811−3815.

(58) Falk, M. *J. Chem. Phys.* **1987**, *86*, 560−564.

(59) Falk, M.; Miller, A. G. *Vib. Spectrosc.* **1992**, *4*, 105−108.

(60) Brill, T. B.; Kieke, M. L.; Schoppelrei, J. W. In Proceedings of the 3rd International Symposium on Supercritical Fluids; Brunner, G., Perrut, M., Eds.; Strasbourg, France, 1994; Vol. 3, p 13.

(61) Eysel, H. H.; Jackson, M.; Mantsch, H. H.; Thomson, G. T. D. *Appl. Spectrosc.* **1993**, *47*, 1519−1521.

Table 2. Solubilities and Half-Width of Absorption Band of ν_2 Mode of CO_2 in Polymers

polymer	CO_2 solubility,[a] g of CO_2/100 g of polymer	$\Delta\nu_{1/2}$,[b] cm^{-1}
PVMK	N/A	18
PVAc	6[c]	16
PEMA	4.8[d]	15
PMMA	4.4[c]	15
PS	3.2[c]	11.5
PE	0.8[e]	5.5

[a] At 25 °C and 14 bar. [b] $\Delta\nu_{1/2}$ = full width at half-maximum of the ν_2 absorption band. [c] From refs 6 and 8. [d] From ref 2e. [e] Hirose, T.; Mizoguchi, K.; Kamiya, Y. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 2107−2115. N/A = not available.

and measured widths are presented in Table 2. Because the ν_2 band has a complicated structure, the different bandwidths in our polymer systems must be viewed as average effective widths only. Table 2 shows that an increase in the width of the ν_2 band parallels the increasing solubility of CO_2. Thus, the solubility of CO_2 in some other basic polymers where the ν_2 band is broad may be high. This prediction would be most applicable at low CO_2 pressures, at the point where all polymer binding sites are not filled by CO_2 (i.e., at or near infinite dilution). However, further investigations of relevant systems are needed. The advantage of this approach is that the sensitivity of ν_2 is sufficient to study CO_2−polymer interactions even when the spectrum of the polymer itself hardly changes.

Conclusions and Implications

The splitting of the ν_2 bending mode of CO_2 signifies the interaction between the polymers and CO_2. Although our investigations have largely focused on splitting of the ν_2 mode of CO_2, the wide range of polymers where this phenomena has been observed (Table 1) makes the spectroscopic evidence for such specific interactions very strong.

Our data are consistent with a specific intermolecular interaction between CO_2 and electron-donating polymer systems, in the form of an electron donor−acceptor complex. This represents the first example of such a specific interaction between gaseous, near-, and supercritical CO_2 with polymers. Our results also suggest that CO_2 in most cases might act as an electron acceptor rather than as an electron donor. This suggestion finds support in other relevant studies. For example, it has been shown recently that CO_2 acts as an electron acceptor toward the oxygen atom of the water which is bound to salt hydrates.[44b] At the same time such interaction may increase the nucleophilicity of CO_2 oxygen atoms, thus, assisting CO_2's ability to bind to metal centers.[62] Similar interactions might provide a plausible explanation for the facilitation of the carbon dioxide insertion into metal−OH bonds.[63] The appreciable Lewis acidity of carbon dioxide is thought to be responsible for the limited aggregation of nonionic surfactants in $scCO_2$[64] and presumably played a major role in the shift of tautomeric equilibrium studied in $scCO_2$.[65] The view of CO_2 as an electron acceptor may well provide additional insight on the solubilities of polymers in liquid and supercritical CO_2. Our findings do not exclude the ability of CO_2 to act as an electron donor in some systems. For an example, it has recently been suggested[66] that the high solubility of poly(dimethylsiloxane) in $scCO_2$ may be due to the interactions of the oxygen electrons of CO_2 with Si atoms in the polymer chains.

Although there are a limited number of polymers that are soluble in $scCO_2$ (fluoropolymers and dimethylsiloxane), some poly(methacrylate)s are also soluble in $scCO_2$.[67] Moreover, Johnston and co-workers[13b] have suggested that the interaction of CO_2 with polymers possessing acrylate groups may be of a Lewis acid−base nature. Even poly(tetrafluoroethylene) can be soluble in $scCO_2$ at high pressures and temperatures,[68] where the interaction of CO_2 with dipoles of C−F bonds may play a role. Stern and co-workers[69] have also proposed specific CO_2−fluorine interactions to explain the increased solubility of CO_2 in polymers containing fluorine groups. Also a rough estimation of the solubility of CO_2 in polymers can, in principle, be obtained from the width of the absorption band of ν_2 mode of CO_2 dissolved in those polymers. Finally, these new results may impact areas as diverse as predictive models for polymer sorption, swelling, plasticization, and permeability and retention in capillary supercritical fluid chromatography.

Acknowledgment. We thank the DuPont Co. for financial support. We also acknowledge Mr. B. West, Mr. D. Bush, Mr. F. Poulliot, Mr. N. B. Brantley, Ms. K. Hafner, and Ms. A. R. Stout for their help and advice.

JA950416Q

---

(62) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259−272.

(63) Sakaki, S.; Musashi, Y. *Inorg. Chem.* **1995**, *34*, 1914−1923.

(64) Harrison, K.; Goveas, J.; Johnston, K. P. *Langmuir* **1994**, *10*, 3536−3541.

(65) O'Shea, K. E.; Kirmse, K. M.; Fox, M. A.; Johnston, K. P. *J. Phys. Chem.* **1991**, *95*, 7863−7867.

(66) Zhao, X.; Watkins, R.; Barton, S. W. *J. Appl. Polym. Sci.* **1995**, *55*, 773−778.

(67) McHugh, M. A.; Krukonis, V. J. *Encyclopedia of Polymer Science and Engineering*; John Wiley & Sons, Inc.: New York, 1989.

(68) Tuminello, W. H.; Dee, G. T.; McHugh, M. A. *Macromolecules* **1995**, *28*, 1506−1510.

(69) Shah, V. M.; Hardy, B. J.; Stern, S. A. *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 313−317.