

# CO–water interactions in argon matrices and in porous ices

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Received 26 August 1996; accepted 6 September 1996

## Abstract

Solid thin layers of Ar/H<sub>2</sub>O/CO and CO/H<sub>2</sub>O mixtures, produced by deposition at cryogenic temperatures, were investigated by FT-IR spectroscopy. The effects of variations in the concentration ratios, deposition temperature and temperature cycling were studied. All observed bands are assigned to either single component or mixed (CO)<sub>m</sub>:(H<sub>2</sub>O)<sub>n</sub> complexes.

Higher deposition temperatures were found to be more effective than temperature cycling of the layers for the production of mixed species. The results indicate that their formation is due more to surface migration of H<sub>2</sub>O than to that of CO molecules.

Conclusions from studies of these films were applied to a study of porous ices produced by temperature cycling of rare gas/H<sub>2</sub>O solid mixtures, onto which CO was deposited as probe. They corroborate that porous ices produced from Ar/H<sub>2</sub>O solid mixtures consist of small ice particles with “surface porosity” and a large proportion of dangling OH bonds. Deposited CO may be attached to more than one OH bond. In contrast, ice thus formed from temperature cycling of Ne/H<sub>2</sub>O solid mixtures has “bulk porosity” with scattered free OH bonds. Deposited CO penetrates these pores to form small solid-like CO clusters or to bond to single OH bonds. © 1997 Elsevier Science B.V.

**Keywords:** CO–water complexes; Infrared spectroscopy; Matrix isolation; Water ices

## 1. Introduction

In a recent study [1], we showed that ice prepared by vapor deposition onto a 5 K substrate is essentially non-porous, with few dangling OH bonds on its surface. Ices with bulk or surface porosity were produced by codeposition or predeposition of inert gases with H<sub>2</sub>O vapors, followed by temperature cycling. The highest amount of dangling OH bonds was found for ices from Ar/H<sub>2</sub>O mixtures. Bulk porosity was associated with Ne/H<sub>2</sub>O samples. Insight was achieved through deposition of CO gas onto the porous ices and the investigation of the CO

infrared bands as well as of the OH stretching mode region.

Further understanding of “CO in porous ice systems” is gained from spectra of inert gas/CO/H<sub>2</sub>O solid mixtures. These were previously investigated in several matrices (O<sub>2</sub>, N<sub>2</sub>, Ar and CO) [2–8] focusing on the CO\*H<sub>2</sub>O dimer. Bands were assigned to the OH and CO stretching modes of this species [2–8], while fewer studies dealt with the H<sub>2</sub>O bending mode of the CO\*H<sub>2</sub>O complex [3,4,6,8].

An ab initio calculation of the CO\*H<sub>2</sub>O complex [9] suggested three structures with a stability order of: OC\*H–OH > CO\*H–OH > T-shaped  $\pi$  complex (“O-bonded”). The spectroscopy is complicated, as both H<sub>2</sub>O and CO monomers retain some rotational

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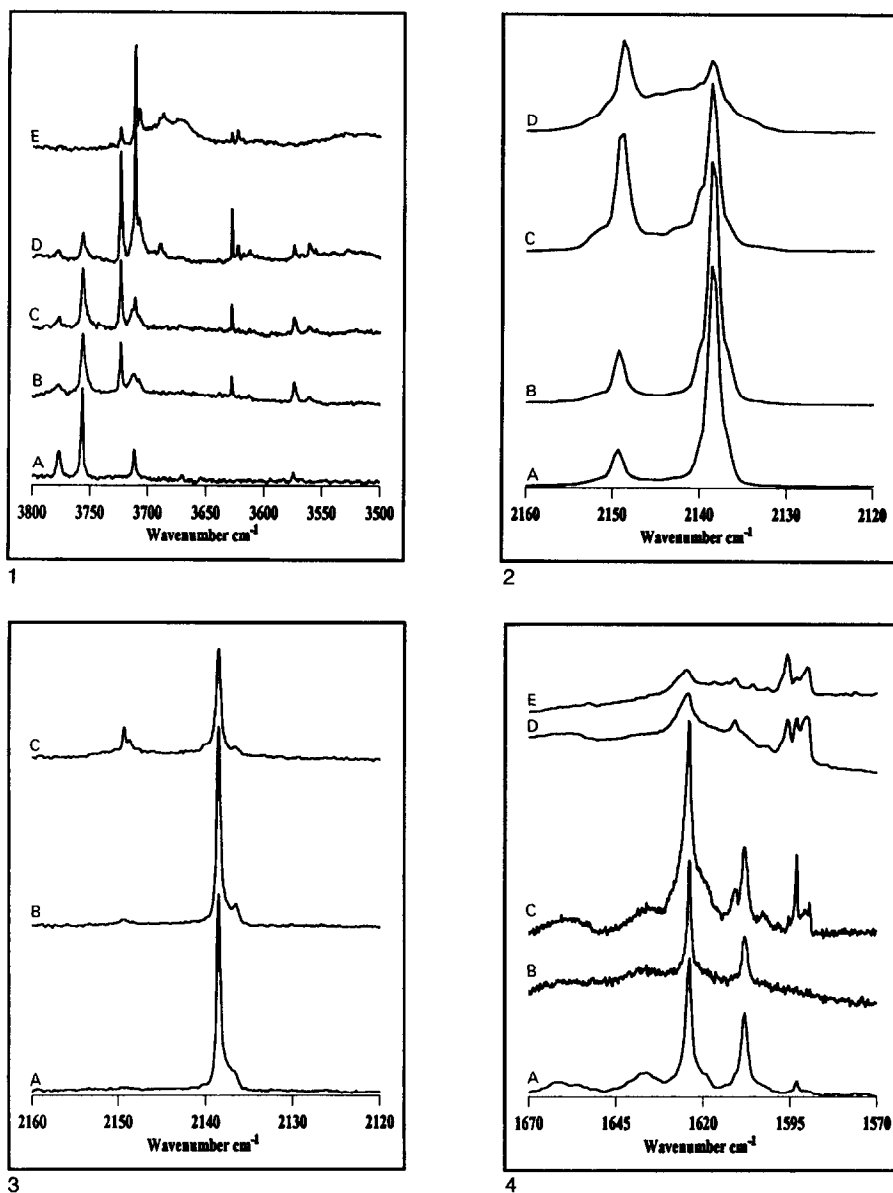
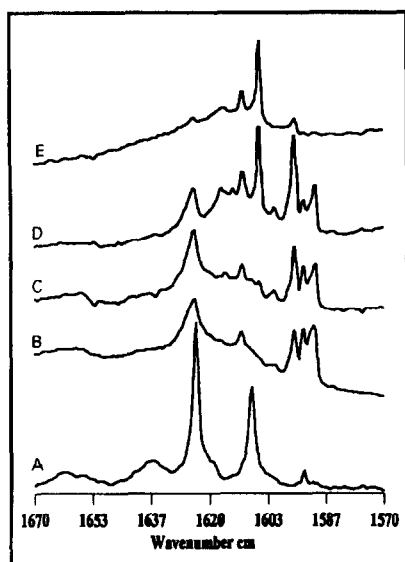


Fig. 1. Effects of deposition temperature in the OH stretch region (recorded at 5 K). (A) 400:1 Ar/H<sub>2</sub>O sample deposited at 5 K (as comparison); 100:1:1 Ar/H<sub>2</sub>O/CO layer deposited at (B) 5 K; (C) 10 K; (D) 15 K; (E) 20 K.

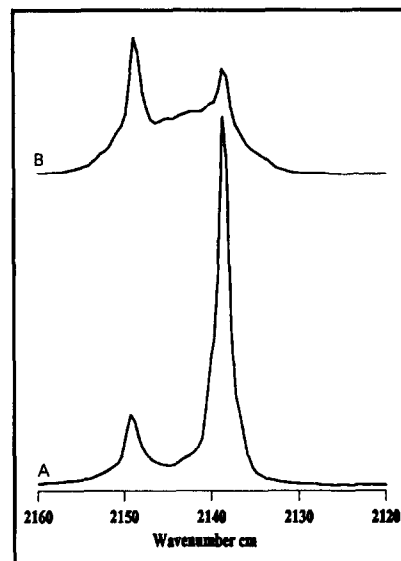
Fig. 2. Effects of deposition temperature on a 100:1:1 Ar/H<sub>2</sub>O/CO solid layer in the CO stretch region (recorded at 5 K). Deposited at (A) 5 K; (B) 10 K; (C) 15 K; (D) 20 K.

Fig. 3. Temperature cycling of a dilute 1000:1:1 Ar/H<sub>2</sub>O/CO solid layer in the CO stretch region (recorded at 5 K). (A) As deposited at 5 K; (B) warmed to 20 K; (C) warmed to 28 K.

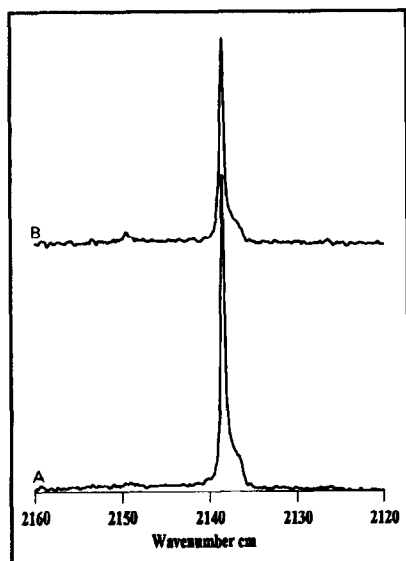
Fig. 4. Effects of concentration changes in the H–O–H bend region (recorded at 5 K). (A) 400:1 Ar/H<sub>2</sub>O sample; (B) 1000:1:1 Ar/H<sub>2</sub>O/CO sample; (C) 2000:1:5 Ar/H<sub>2</sub>O/CO sample; (D) 100:1:1 Ar/H<sub>2</sub>O/CO sample; (E) 100:1:2 Ar/H<sub>2</sub>O/CO sample.



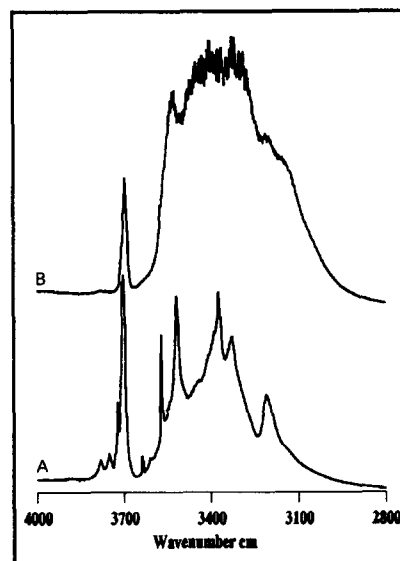
5



6



7



8

Fig. 5. Effects of deposition temperature in the H–O–H bend region (recorded at 5 K). (A) 400:1 Ar/H<sub>2</sub>O sample deposited at 5 K (as comparison); 100:1:1 Ar/H<sub>2</sub>O/CO layer deposited at (B) 5 K; (C) 10 K; (D) 15 K; (E) 20 K.

Fig. 6. Deposition temperature vs. temperature cycling effects on CO\*H<sub>2</sub>O formation in a 100:1:1 Ar/H<sub>2</sub>O/CO solid layer in the CO stretch region (recorded at 5 K): (A) deposited at 5 K, cycled to 20 K; (B) deposited at 20 K.

Fig. 7. H<sub>2</sub>O concentration effects on CO\*H<sub>2</sub>O formation in the CO stretch region (recorded at 5 K). (A) 1000:1:1 Ar/H<sub>2</sub>O/CO sample; (B) 2000:5:1 Ar/H<sub>2</sub>O/CO sample.

Fig. 8. Effects of temperature cycling on a 4:1 Ar/H<sub>2</sub>O solid layer in the OH stretch region (recorded at 5 K). (A) As deposited at 5 K; (B) warmed to 40 K.

Table 1  
Band assignments and frequencies for ternary Ar:H<sub>2</sub>O:CO solid mixtures

Species	Band frequencies (cm <sup>-1</sup> ) and assignments	Figure numbers for relevant spectra
H <sub>2</sub> O (monomer)	$\nu_3$ 3776, 3756, 3711 $\nu_1$ 3670	1A 1A
(H <sub>2</sub> O) <sub>2</sub>	$\nu_2$ 1660, 1636, 1624, 1607 $\nu_3$ 3708 $\nu_1$ 3574	4A, 5A 1B,C,D 1A,B,C,D
(H <sub>2</sub> O) <sub>3</sub>	$\nu_2$ 1611, 1593 $\nu_3$ 3612 $\nu_1$ 3560 (?), 3520 $\nu_2$ 1613(?), 1602, 1589	5B,C 1D,E 1D,E 5D,E
CO (monomer)	2138.5, 2137 (unstable site) 2088 ( <sup>12</sup> C <sup>18</sup> O), 2091 ( <sup>13</sup> C <sup>16</sup> O)	3A,B,C; 6A,B; 7A,B
(CO) <sub>2</sub>	2140	3A,B,C
(CO) <sub>n</sub>	2133, 2137 2C,D	
CO*H <sub>2</sub> O	$\nu_3$ 3723 (H-bonded), 3711 (O-bonded) $\nu_1$ 3627 (H-bonded) $\nu_2$ 1595 $\nu$ (CO) 2149.3 (H-bonded), 2148.6, 2102 ( <sup>13</sup> C <sup>16</sup> O)	1B,C,D,E 1B,C,D,E 5B,C,D,E 2A,B,C,D; 3B,C; 6A,B; 7B
CO(H <sub>2</sub> O) <sub>2</sub>	$\nu_3$ 3711, 3689 $\nu_1$ 3622, 3561, 3555 $\nu_2$ 1616, 1605 $\nu$ (CO) 2153	1D,E 1D,E 5D,E 2C,D
(CO) <sub>2</sub> H <sub>2</sub> O	$\nu_3$ 3708 $\nu_1$ 3618 $\nu_2$ 1611 $\nu$ (CO) 2142	1D,E 1D,E 5D,E 2C,D
(CO) <sub>2</sub> (H <sub>2</sub> O)	$\nu_3$ 3690 ( $n > m$ ), 3672 ( $m > n$ ) $\nu_1$ 3520 $\nu$ (CO) 2151 ( $n > m$ ), 2145 ( $m > n$ )	1E 1E 2D

freedom and their low molecular weights allow thermal motion to form polymeric CO<sub>m</sub>(H<sub>2</sub>O)<sub>n</sub> species.

## 2. Experimental

Ar (5.7) and CO (4.7) gases were used. Water vapor was taken from deionized water after degassing cycles. Samples were deposited onto a Kel-F coated CsI window, maintained at 5 K by an Air Products HS-4 Heliplex. Deposition times ranged from 40 min to 4 h. Temperature cycling of the samples by a slow warming (1 K min<sup>-1</sup>) was followed by quick recooling to 5 K. Spectra were recorded on a Bruker IFS 88 employing a DTGS detector.

## 3. Results and discussion

Infrared bands of species from Ar:H<sub>2</sub>O:CO mixtures belong to three main regions:

1. the OH stretching region, 4000–2700 cm<sup>-1</sup>;
2. the CO stretching region, 2200–2000 cm<sup>-1</sup>;
3. the H<sub>2</sub>O bending mode region, 1700–1500 cm<sup>-1</sup>.

A summary of assignments, based upon experiments involving variations in relative concentrations, deposition temperatures and temperature cycling is given in Table 1. Relevant spectra are reproduced in Figs. 1–8. Assignments of the higher mixed multi-mers are first presented here. We note that the CO bands at 2148 cm<sup>-1</sup> and 2138.2 cm<sup>-1</sup> are essentially identical to those for CO in porous ice [1], in support

of our contention that in such ice, CO is either present in solid clusters (“S”-band) or is bonded to single scattered dangling OH bonds (“H” band).

### Acknowledgements

A Short Term EERO Fellowship to A.L. at the University of Oslo, is acknowledged.

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