

The adsorption of acetone on non-porous and meso-porous silica

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Supporting Information

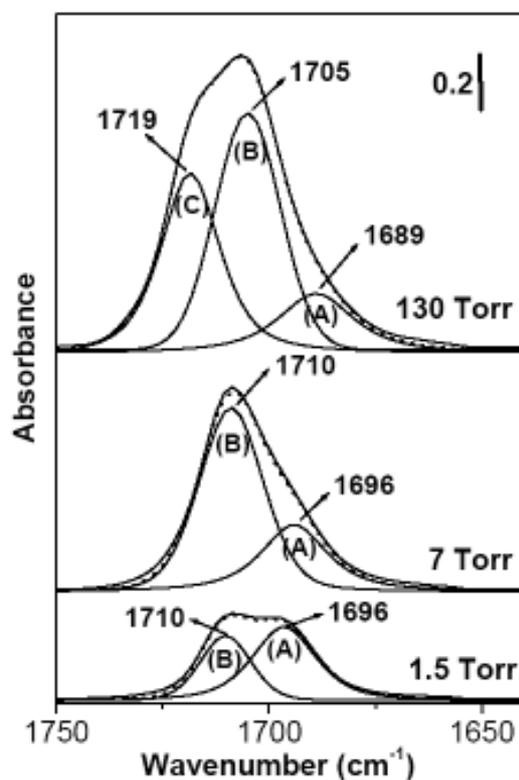


Figure 1SM - Computer spectral resolution of the absorbance spectra in the ν_{CO} spectral range (after subtraction of the contribution due to the gaseous phase) of acetone adsorbed onto a thin-pellet sample of A303 under equilibrium pressures 1.5, 7, and 130 Torr. Upper solid lines: experimental spectra; upper broken lines: simulated spectra; curves (A), (B), and (C): computer resolved components.

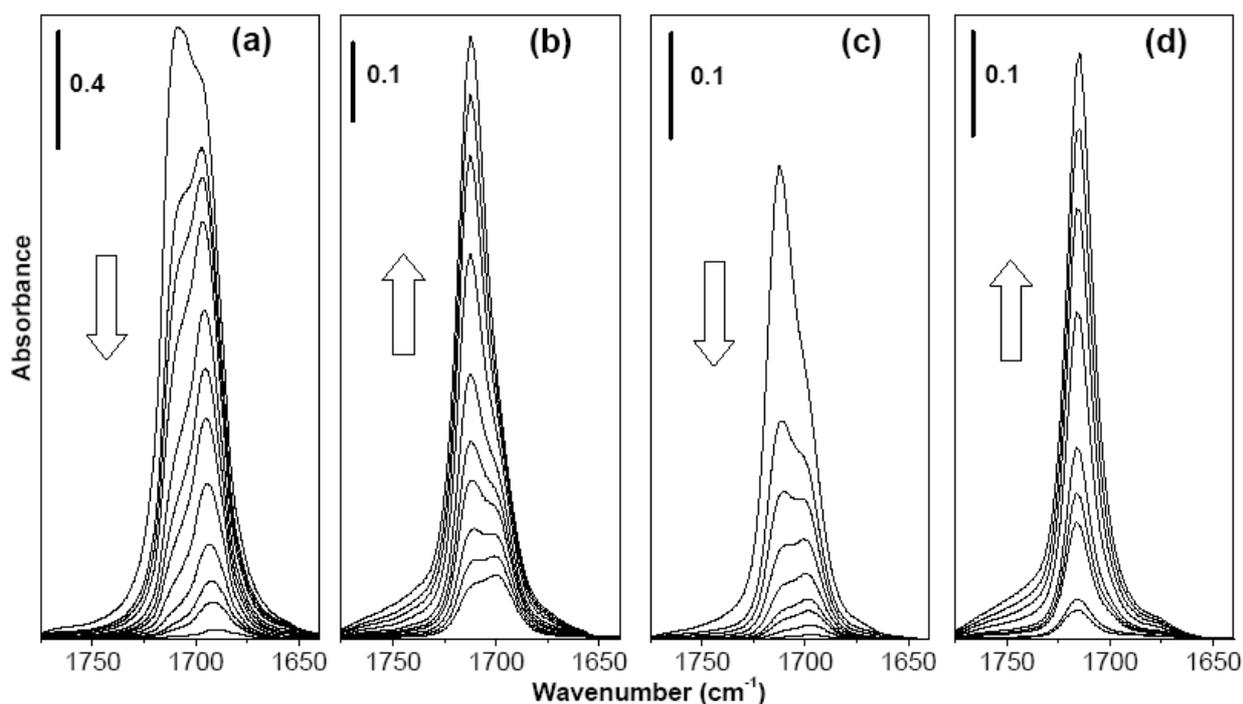


Figure 2SM - Mass-normalized absorbance spectral patterns in the ν_{CO} spectral range of acetone adsorbed/desorbed on the three *AT* samples. Section (a): desorption pattern of *A303* (main aspects of the corresponding adsorption pattern are presented in fig. 7 and 1SM). Top-to-bottom, evacuation times (sec) are: 1, 3, 5, 10, 20, 40, 60, 120, 240, 480, 720, 1800; Sections (b) and (c): adsorption and desorption pattern of *A673*. In (b), equilibrium pressures (Torr) are: 0.1, 0.2, 0.3, 0.5, 0.7, 1, 2, 3, 4, 5. In (c), evacuation times (sec) are: 1, 3, 5, 10, 20, 40, 60, 120, 240; Section (d): adsorption pattern of *A1100*. (The corresponding “one-peak” desorption pattern is not shown, as virtually coincident with the apparently “one-peak” adsorption one. In fact, only computer resolution allows to evidence the presence, also on *A1100*, of minor amounts of the *A* acetone component). In (d), equilibrium pressures (Torr) are: 0.1, 0.3, 0.5, 0.7, 1, 2, 3, 4, 5.

Table 1SM

Selected spectral features of the resolved components of acetone adsorbed on A303 (thin pellet)

p (Torr)	Spectral features (cm ⁻¹)	A	B	C
0.5	ν_{\max}	1696.1	1710.2	-
	$\Delta\nu_{1/2}$	16.9	13.7	-
	A_{int}	3.96	1.74	-
1	ν_{\max}	1696.3	1710.3	-
	$\Delta\nu_{1/2}$	17.2	13.8	-
	A_{int}	4.47	2.40	-
1.5	ν_{\max}	1696.4	1710.2	-
	$\Delta\nu_{1/2}$	17.4	13.9	-
	A_{int}	4.92	3.11	-
2	ν_{\max}	1696.5	1710.2	-
	$\Delta\nu_{1/2}$	17.7	14.1	-
	A_{int}	5.47	3.53	-
5	ν_{\max}	1696.9	1710.2	-
	$\Delta\nu_{1/2}$	18.7	14.3	-
	A_{int}	5.92	5.23	-
7	ν_{\max}	1695.9	1709.6	-
	$\Delta\nu_{1/2}$	18.6	15.8	-
	A_{int}	5.46	7.75	-
10	ν_{\max}	1694.1	1708.9	-
	$\Delta\nu_{1/2}$	18.4	17.8	-
	A_{int}	4.36	10.53	-
13	ν_{\max}	1694.7	1709.1	1724.4
	$\Delta\nu_{1/2}$	19.4	16.7	9.1
	A_{int}	5.53	9.47	0.47
20	ν_{\max}	1693.7	1708.7	1723.9
	$\Delta\nu_{1/2}$	19.7	17.7	10.6
	A_{int}	5.0	10.81	0.7
24	ν_{\max}	1693.3	1708.6	1723.5
	$\Delta\nu_{1/2}$	20.1	18.0	11.1
	A_{int}	4.87	11.31	0.85
30	ν_{\max}	1692.3	1708.3	1722.9
	$\Delta\nu_{1/2}$	20.5	18.7	11.9
	A_{int}	4.51	12.24	1.1
40	ν_{\max}	1690.9	1707.8	1722.1
	$\Delta\nu_{1/2}$	21.2	19.6	12.7
	A_{int}	4.08	13.43	1.61
50	ν_{\max}	1689.9	1707.6	1721.8
	$\Delta\nu_{1/2}$	22.4	20.4	12.2
	A_{int}	3.94	14.34	1.74
70	ν_{\max}	1689.4	1707.1	1720.9
	$\Delta\nu_{1/2}$	21.4	20.1	14.4
	A_{int}	3.63	14.21	3.16
90	ν_{\max}	1688.7	1706.6	1720.2
	$\Delta\nu_{1/2}$	21.3	20.0	15.3
	A_{int}	3.49	14.16	4.63
110	ν_{\max}	1686.7	1706.4	1720.2
	$\Delta\nu_{1/2}$	21.0	21.4	15.0
	A_{int}	3.80	15.69	4.90
130	ν_{\max}	1686.0	1705.0	1718.6
	$\Delta\nu_{1/2}$	21.1	18.0	16.6
	A_{int}	4.01	15.20	8.09

Table 2SM

Selected spectral features of the resolved components of the early stages of acetone adsorption on MCM303

p (Torr)	Spectral features (cm ⁻¹)	A	B	C
0.001	ν_{\max}	1690.8	1706.6	-
	$\Delta\nu_{1/2}$	15.2	13.4	-
	A_{int}	0.95	0.12	-
0.005	ν_{\max}	1691.0	1707.9	-
	$\Delta\nu_{1/2}$	17.2	11.2	-
	A_{int}	5.82	0.34	-
0.02	ν_{\max}	1691.7	1707.9	-
	$\Delta\nu_{1/2}$	17.4	11.2	-
	A_{int}	11.9	0.80	-
0.06	ν_{\max}	1692.2	1707.7	-
	$\Delta\nu_{1/2}$	17.6	11.9	-
	A_{int}	17.8	1.62	-
0.1	ν_{\max}	1692.4	1707.5	-
	$\Delta\nu_{1/2}$	17.9	12.5	-
	A_{int}	21.97	2.41	-
0.2	ν_{\max}	1692.5	1707.0	-
	$\Delta\nu_{1/2}$	18.1	13.6	-
	A_{int}	25.43	3.79	-
0.3	ν_{\max}	1691.8	1705.1	-
	$\Delta\nu_{1/2}$	18.6	16.6	-
	A_{int}	30.15	10.78	-
0.5	ν_{\max}	1690.2	1702.9	1709.9
	$\Delta\nu_{1/2}$	18.8	14.1	13.4
	A_{int}	34.12	13.29	9.68
0.7	ν_{\max}	1690.7	1700.8	1709.8
	$\Delta\nu_{1/2}$	20.3	13.4	13.1
	A_{int}	41.27	15.17	16.75
1	ν_{\max}	1690.6	1700.6	1709.8
	$\Delta\nu_{1/2}$	20.9	13.4	13.0
	A_{int}	41.18	16.44	19.45
1.7	ν_{\max}	1690.4	1700.6	1710.4
	$\Delta\nu_{1/2}$	22.1	14.1	13.2
	A_{int}	42.54	17.15	21.03
3	ν_{\max}	1689.4	1700.6	1710.9
	$\Delta\nu_{1/2}$	21.8	16.7	15.1
	A_{int}	38.96	22.11	24.25

Table 3SM

Selected spectral features of the resolved components of the early stages of acetone adsorption on MCM673

p (Torr)	Spectral features (cm ⁻¹)	A	B
0.01	ν_{\max}	1695.8	1710.4
	$\Delta\nu_{1/2}$	15.0	13.6
	A_{int}	3.81	1.39
0.03	ν_{\max}	1696.5	1710.6
	$\Delta\nu_{1/2}$	15.6	13.1
	A_{int}	9.56	3.95
0.07	ν_{\max}	1696.7	1710.6
	$\Delta\nu_{1/2}$	15.9	13.0
	A_{int}	14.11	6.71
0.1	ν_{\max}	1696.9	1710.5
	$\Delta\nu_{1/2}$	16.5	13.0
	A_{int}	19.64	11.04
0.2	ν_{\max}	1696.9	1710.5
	$\Delta\nu_{1/2}$	16.8	13.1
	A_{int}	22.71	14.04
0.3	ν_{\max}	1696.8	1710.6
	$\Delta\nu_{1/2}$	17.4	13.4
	A_{int}	27.72	18.54
0.5	ν_{\max}	1696.7	1711.2
	$\Delta\nu_{1/2}$	18.4	14.2
	A_{int}	31.92	23.12
0.7	ν_{\max}	1696.7	1711.7
	$\Delta\nu_{1/2}$	19.0	14.6
	A_{int}	34.47	24.30
1	ν_{\max}	1696.7	1712.4
	$\Delta\nu_{1/2}$	19.7	15.1
	A_{int}	37.08	24.98
2	ν_{\max}	1696.7	1713.3
	$\Delta\nu_{1/2}$	20.8	15.8
	A_{int}	39.9	25.59
3	ν_{\max}	1696.8	1714.0
	$\Delta\nu_{1/2}$	21.6	16.4
	A_{int}	41.81	26.00

Passing from resolved optical isotherms to resolved quantitative isotherms

Needless to say, the easiest way to pass from total-and-resolved spectroscopic isotherms to total-and-resolved quantitative isotherms is to assume that the two acetone adspecies A and B possess the same molar extinction coefficient although, in principle, this assumption is not correct. In fact, two distinct IR bands, corresponding to the same vibrational mode of two distinct adsorbed species, should derive from two distinct vibrational transition moments.¹

Actually, having more than one (total) quantitative adsorption isotherm, relative to differently activated *AT* systems, a two-equations system having as unknowns the two extinction coefficients could be resolved, and yield the real individual contributions of the two acetone adspecies A and B to the build-up of overall (spectroscopic) isotherms. But we know from previous experience, concerning different adsorbates that yield, like in the present case, two or more closely overlapped bands (*e.g.*, the RT/BT adsorption of CO on several d^0 oxides, dealt with by some of us some years ago), that the accuracy of individual extinction coefficients obtained in this way is rather poor.

Alternatively, one could ascribe the whole lower quantitative isotherm of fig. 1a (overall acetone uptake on *A1100*) to the sole B acetone species, ignoring the (minor) contribution of species A that still forms on the highly dehydrated *A1100* system. This procedure has been actually tried, and the results obtained turned out to be only slightly different (though, obviously, relative only for the two resolved *A303* and *A673* systems) from those obtained assuming, for each one of the three *AT* systems, the same extinction coefficient for acetone adspecies A and B.

On the other hand, the latter simplifying assumption, although wrong in principle, should not be so wrong in numerical terms, since: - ν_{CO} vibrations of saturated aliphatic ketones are known to possess fairly high specific intensities [*e.g.*, see ref. (2)], so that relatively small changes of extinction coefficient are bound to count very little in percent terms; - A and B adspecies correspond to acetone molecules adsorbed in the same way (*i.e.*, by CO/OH H-bonding), so that no large differences of dipole moment changes³ should be expected for the two ν_{CO} vibrations; - the

two ν_{CO} vibrations absorb at very close spectral positions, so that (at least) the important part of the integrated absorption coefficient that is frequency-dependent⁴ should be expected to be virtually the same in the two cases.

For all these reasons, of both experimental and spectroscopic nature, we think that the assumption of the same molar extinction coefficient for the ν_{CO} mode of species A and B should not introduce a dramatic error in the evaluation of A and B surface concentrations.

References

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