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Supplementary Material

"Reactive and non-reactive species formed during the methanolysis of $NaBH_4$: A theoretical and experimental approach"

By

Alejandro Vallejo Orrego [a], Cristián A. Ferretti [b] and Verónica K. Díez [a]*

[a] Catalysis Science and Engineering Research Group (GICIC), INCAPE, UNL-CONICET, CCT CONICET Santa Fe, Colectora Ruta Nac. 168, km 0, Paraje "El Pozo", (3000) Santa Fe, Argentina

[b] Fester Laboratory of Organic Chemistry, Institute of Applied Chemistry of Litoral, IQAL, UNL-CONICET, Santiago del Estero 2829, (3000) Santa Fe, Argentina

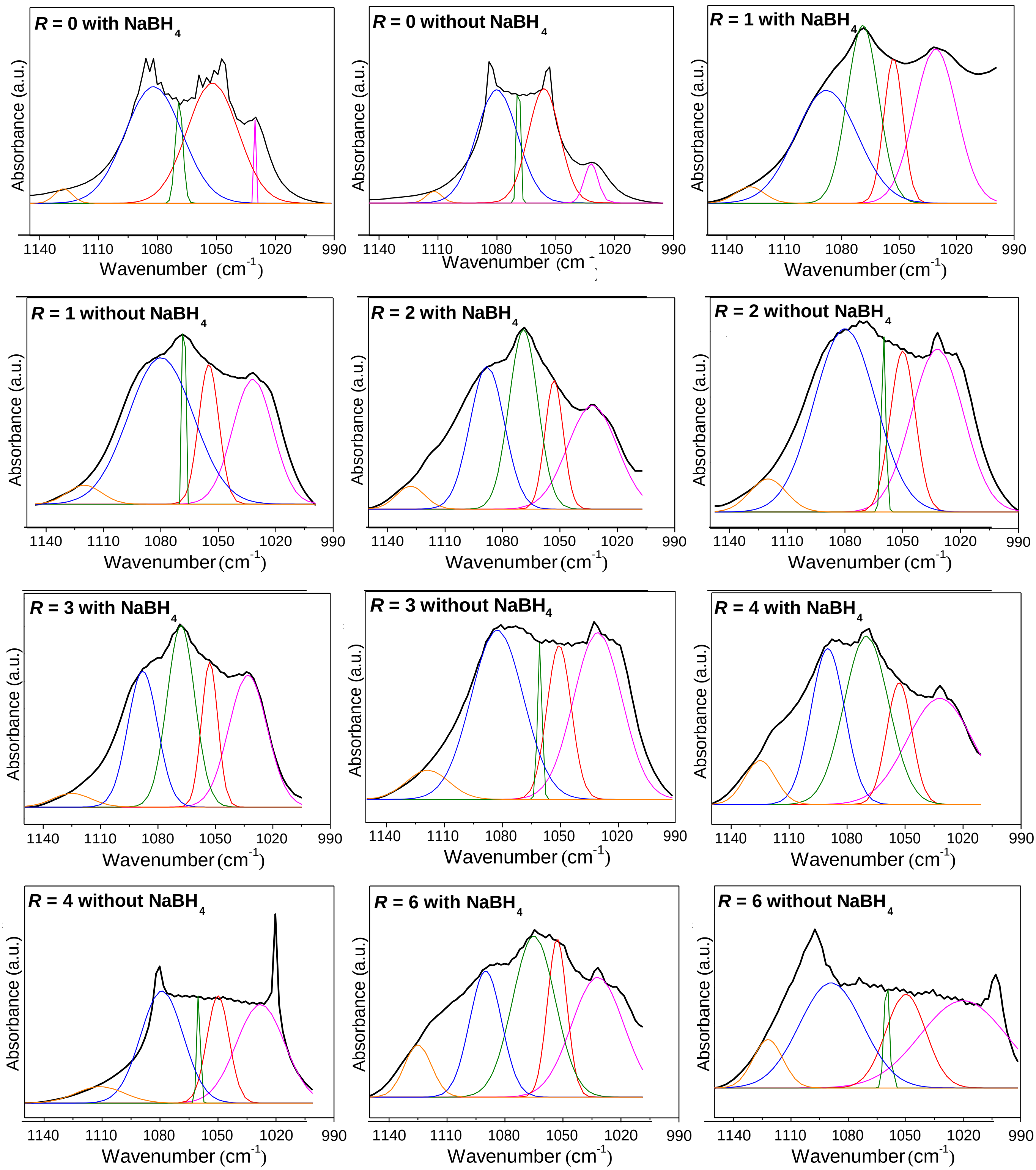
*Corresponding author. Tel.: +54-342-4571164, Ex 2554; Fax: +54-342-4571162.
E-mail address: cferretti@fiq.unl.edu.ar (C.A. Ferretti)

Caption to Figures

Figure S1. Deconvolutions carried out for liquid samples obtained from $NaBH_4$ methanolysis tests performed with and without $NaBH_4$ for with *R* ratios varying from 0 to 6 (*R*=0 with $NaBH_4$ corresponds to a $NaBH_4$/THF solution and *R*=0 without $NaBH_4$ corresponds to pure THF).

Figure S2. Evolution of Y for 1053 cm^{-1} and 1090 cm^{-1} (THF ring strain) bands for liquid samples as a function of *R* for methanolysis tests carried out with and without $NaBH_4$.

Figure S3. Effect of the presence of the methanol solvent on the theoretical IR spectra of the different anionic (A) and neutral (B) species.



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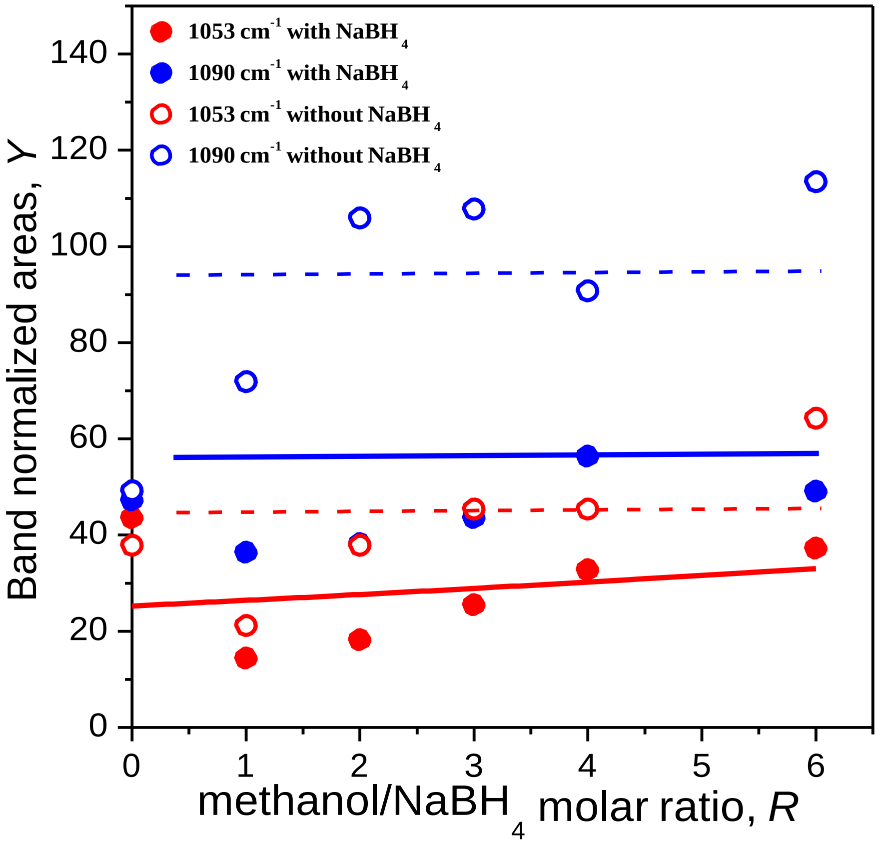

Figure S2. Evolution of *Y* for 1053 cm^{-1} and 1090 cm^{-1} (THF ring strain) bands for liquid samples as a function of *R* for methanolysis tests carried out with and without $NaBH_4$.

Table S1. Theoretical calculations of the interaction of neutral species with methanol.

Reacción	**ΔE (Kcal/mol)**
$Na[BH_4] + CH_3OH \rightarrow Na[BH_3(OCH_3)] + H_2$	175.89
$Na\ BH_3(OCH_3)] + CH_3OH \rightarrow Na[BH_2(OCH_3)_2] + H_2$	135.05
$Na[BH_2(OCH_3)_2] + CH_3OH \rightarrow Na[BH(OCH_3)_3] + H_2$	147.68
$Na[BH(OCH_3)_3] + CH_3OH \rightarrow Na[B(OCH_3)_4] + H_2$	147.83

[a] calculated by Eq. 5

Table S2. Assignments obtained from DFT calculations of vibrational modes of bonds present in the species studied.

Assignments	Anionic species					Neutral species				
	$[BH_4]^-$	$[BH_3(OCH_3)]^-$	$[BH_2(OCH_3)_2]^-$	$[BH(OCH_3)_3]^-$	$[B(OCH_3)_4]^-$	$NaBH_4$	$Na[BH_3(OCH_3)]$	$Na[BH_2(OCH_3)_2]$	$Na[BH(OCH_3)_3]$	$Na[B(OCH_3)_4]$
$\nu(\mathbf{C-H_3})_{\mathbf{as}}$	-	2846-2768	2870-2863	2879-2876	2888-2879	-	2959-2871	2968-2936	2982-2944	2969-2931
$\nu(\mathbf{C-H_3})_{\mathbf{s}}$	-	2765	2844	2848-2846	2837-2833	-	2839	2862-2858	2892-2869	2886-2882
$\nu(\mathbf{C-H})$	-		2781	2806-2801	2818-2814	-		2904	2866	2869
$\nu(\mathbf{B-H})$	2159-2157	2219-2063	2161-2030	2024	-	2176-2144	2142-1926	2128-2003	2082	-
$\delta(\mathbf{C-H_3})_{\mathbf{as}}$	-	1446	1453-1450	1458-1454	1459	-	1450	1459-1454	1464-1455	1469-1454
$\delta(\mathbf{C-H_3})_{\mathbf{s}}$	-	1413	1423-1411	1425	1420	-	1435-1429	1439-1422	1442-1420	1442-1422
$\nu(\mathbf{B-O}_{\boldsymbol{n}})$	-	-	1167	1168	1183-1169	-	1292	1184-1165	1191-1162	1188-1164
$\rho(\mathbf{C-H_3})$	-	1131	1134	1135	1137	-	1133	1138	1138	1138
$\delta(\mathbf{B-H})$	1036	1120-1107	1131-1086	1133-1077	-	1140-1077	1034-1030	1135-1063	1153-1103	-
$\nu(\mathbf{C-O})$	-	1097	1104	1110	1098-1085	-	1130	1046	1068-1018	1121-1098
$\delta(\mathbf{B-O})$	-	925-915	919-838	880	950	-	1194-1172	1157-1115	1087-942	1050-1021
$\nu(\mathbf{B-O})$	-	777	794	880	892	-	920	896-712	775	878-863
$\nu(\mathbf{B--Na})$	-	-	-	-	-	419	303	308	315	315

S3. Theoretical evaluation of vibrational frequencies with the effect of the solvent

It is known that the presence of a given medium on a species, acting as a solvent, gives them an environment that fundamentally affects the vibrational modes of the bonds in the species. To evaluate the effect of the solvent on the vibration frequencies of the species in anionic and neutral forms, theoretical calculations were carried out to analyze the influence of the presence of methanol on said species. Figure S3 shows the spectra of the different anionic and neutral species, in the absence and the presence of methanol. When analyzing the spectra of the anionic and neutral species, it is observed that regardless of the dielectric constant of the solvent, slight shifts of the main assignments of the vibration modes of the bonds are produced in all cases. Generically, both for the anionic species and the neutral species, it is observed in all cases that the assignments present at frequencies higher than 2000 cm^{-1} present shifts towards higher frequencies; while the assignments present at frequencies lower than 2000 cm^{-1} show a shift towards lower frequencies, except in the case of the $[BH_4]^-$ and $NaBH_4$ species. For anionic species, the shifts from solvent-free assignments are ≈ 1-56 cm^{-1}; while for neutral species these shifts present values of ≈ 1-108 cm^{-1}. These shifts correspond to the range of modifications to be found in experimental tests carried out under different procedures and are of the order that can be found when evaluating different species in polar and protic solvents [1]. A very clear fact is presented when analyzing the effect of the solvent on the assignments, that qualitatively a notable increase in the intensity of the assignments is observed.

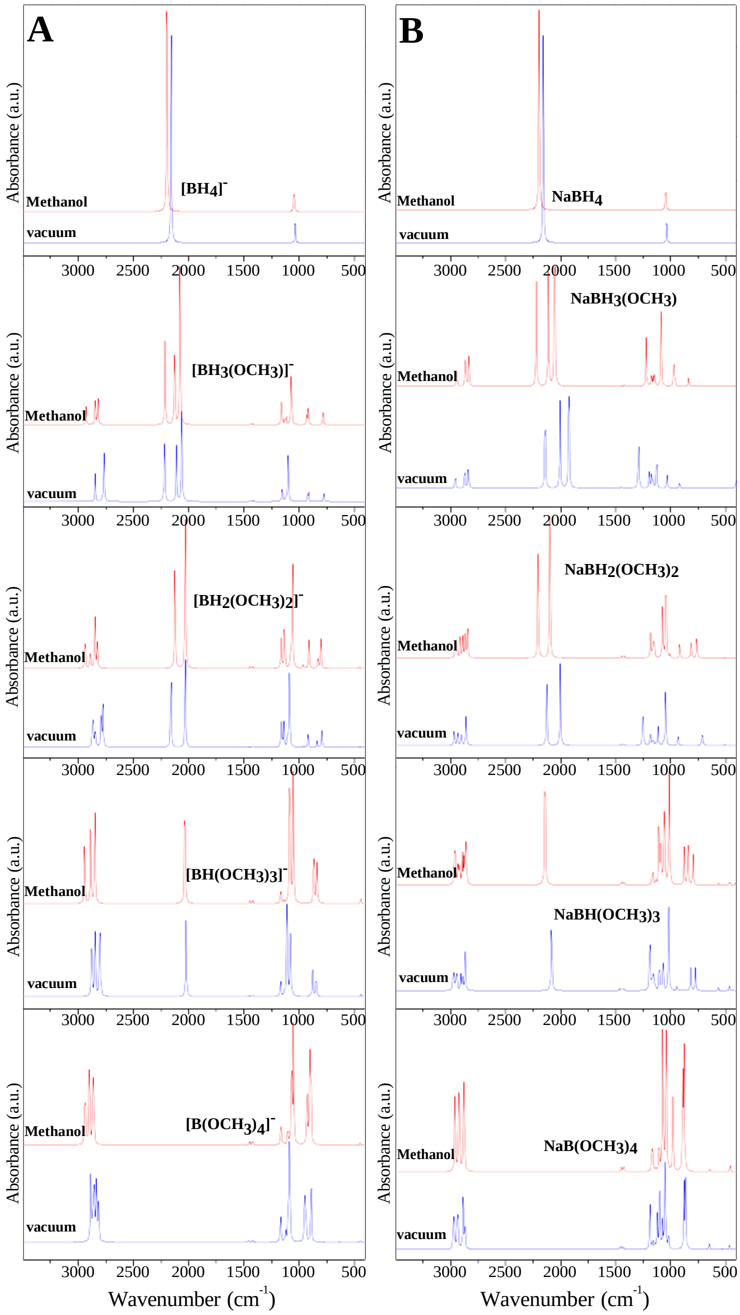

Figure S3. Effect of the presence of the methanol solvent on the theoretical IR spectra of the different anionic (A) and neutral (B) species.

References

[1] J.B. Foresman , Ae. Frisch, Exploring Chemistry With Electronic Structure Methods, 3hd ed., Gaussian Inc., Wallingford, CT, 2015.