SUPPORTING INFORMATION

Influence of multiple protonation on the initial excitation in a black dye

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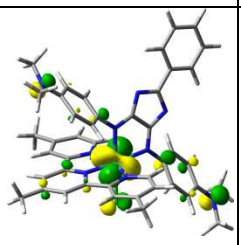
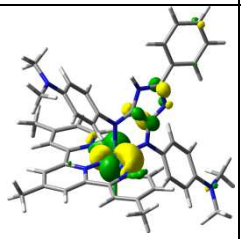
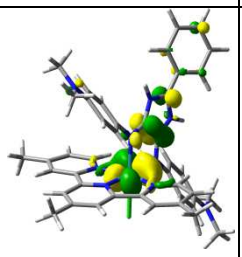
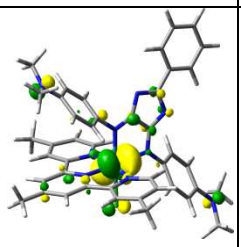
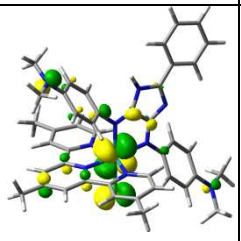
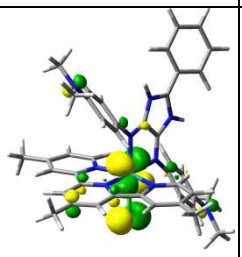
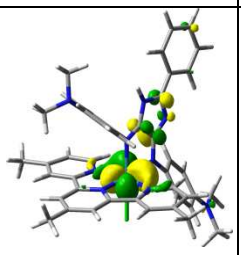
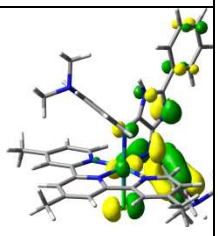
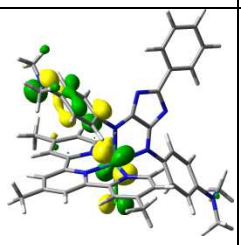
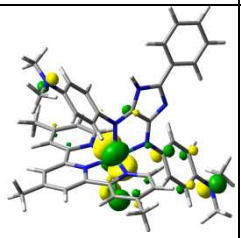
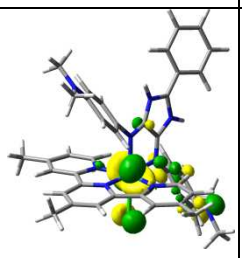
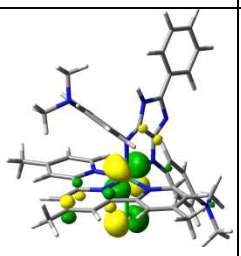
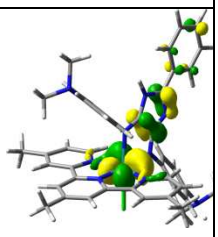
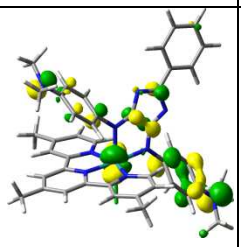
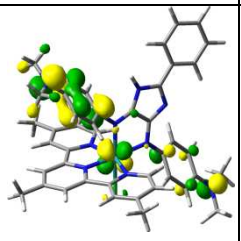
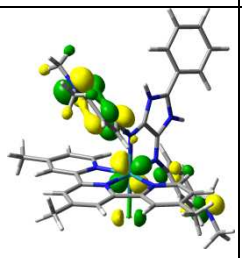
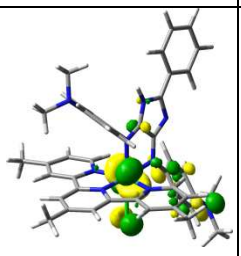
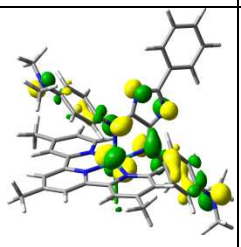
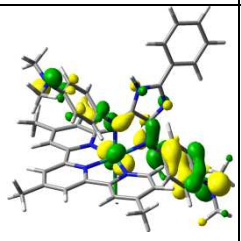
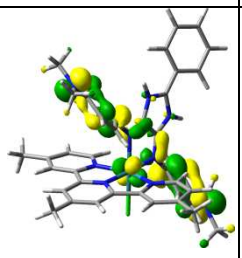
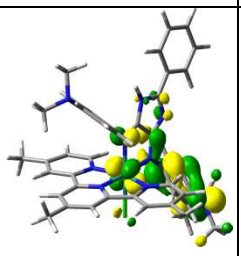
Table S1: Molecular orbitals involved in the main configurations of the states responsible for the absorption and RR properties

	Ru	**RuH**	**RuH_2imim**	**RuH_2imam**	**RuH_3**
194					
195					
196					
197					
198					

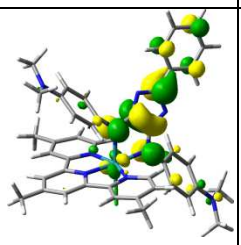
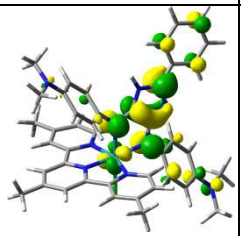
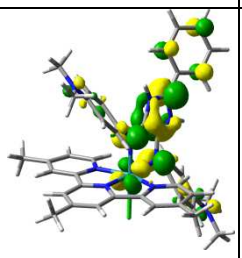
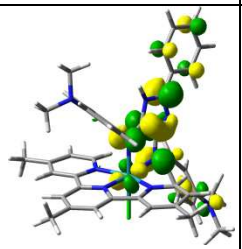
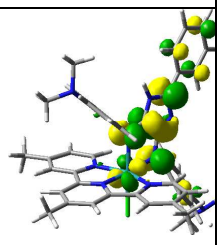
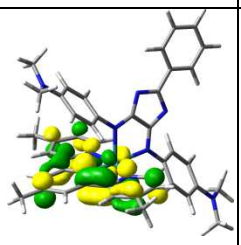
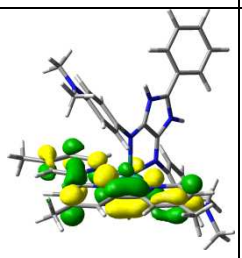
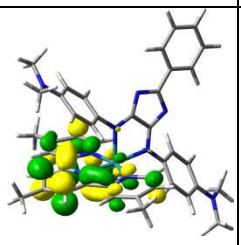
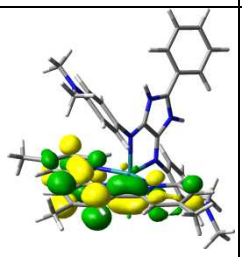
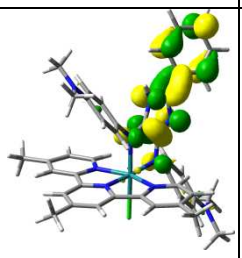
	Ru	**RuH**	**RuH_2imim**	**RuH_2imam**	**RuH_3**
199					
200					
201					
202					

Table S1: Assignment of the vibrational frequencies (cm^{-1}) to molecular substructures. The theoretical frequencies were scaled by a factor of 0.97. Regions dominated by solvent bands are indicated by Solv.

$[(tbterpy)_2 Ru]^{2+}$	**Ru**		**RuH**		**RuH_2imam**	**RuH_3**	
Freq.exp. /cm^{-1}	**Freq.cal. /cm^{-1}**	**Freq.exp. /cm^{-1}**	**Freq.cal. /cm^{-1}**	**Freq.exp. /cm^{-1}**	**Freq.cal. /cm^{-1}**	**Freq.cal. /cm^{-1}**	**Freq.exp. /cm^{-1}**
					1647(im)	1656(im)	1635
1612	1615(im)	1610	1639(im)		1611(im)	1610(im)	
	1609(tbterpy)		1606(im)	1604	1606(im)	1606(im)	1605
	1592(im)	1595					
	1577(im)	1578				1586(im)	1585
						1570(im)	1568
	1564(im)	1558	1552(im/ tbterpy)	1558	1544(im/ tbterpy)		
	1549(im/ tbterpy)		1547(im/ tbterpy)				
1536	1536(tbterpy)	1535					
1518	1516(im)						
						1510(im)	1511
			1504(im)	1504	1502(im)	1505(im)	
	1492(im)	1492	1498(im)		1493(im)		
1481	1473(tbterpy)		1477(im/ tbterpy)	1476	1475(im/ tbterpy)	1476(im/ tbterpy)	1478
	1467(tbterpy)				1460(im)		
1448			1449(im)	1453	1448(im)	1449(im)	1456
			1440(im/ tbterpy)				
	1437(tbterpy)	1442	1439(im/ tbterpy)				
	1399(tbterpy)		1387(im)	1411	1392(im/ tbterpy)	1392(tbterpy)	1398
	1390(tbterpy)				1385(im)	1385(im)	
	1379(im)	1386					
		Solv		Solv			Solv
	1360(im)						
	1349(im)						
	1336(im)	1357	1342(im)		1331(im)	1334(im)	1349
1327	1323(tbterpy)	1328	1326(tbterpy)	1329	1326(tbterpy)	1327(im)	
			1304(im)	1314	1306(im)	1304(im)	1318
1296			1284(im/ tbterpy)		1283(im)	1289(im)	
1280							
1271							
1250		1248		1260	1255(im)	1255(im)	1260
	1234(im)	1242	1253(im)	1236	1228(im)		
					1223(im)	1218(im)	1226
1207							
	1180(im)	1183	1190(im)		1187(im)	1183(im)	1183

$[(tbterpy)_2Ru]^{2+}$	**Ru**		**RuH**		**RuH_2imam**	**RuH_3**	
Freq.exp. /cm^{-1}	**Freq.cal. /cm^{-1}**	**Freq.exp. /cm^{-1}**	**Freq.cal. /cm^{-1}**	**Freq.exp. /cm^{-1}**	**Freq.cal. /cm^{-1}**	**Freq.cal. /cm^{-1}**	**Freq.exp. /cm^{-1}**
			1179(im)	1184	1179(im)	1176(im)	
	1162(im)	1168	1172(im)		1173(im)		
		1131	1147(im)	1149	1149(im)	1148(im)	1154
	1119(im)	1120					
		1076	1075(tbterpy)	1083	1075(tbterpy)		1080
			1057(im)	1066	1050(im)		
	1073(tbterpy)	1046	1030(im/ tbterpy)	1046	1031(im/ tbterpy)		1046
1017	1005(tbterpy)	1002	985(im)	1002	985(im)		1014
	950(im)	959	937(im)	956	934(im)	950(im)	963
	929(tbterpy)	Solv			924(im)	932(tbterpy)	
		Solv	919(im)	Solv			Solv
904	922(im)	903	910(im)	903	910(im)	910(im)	
	866(im)	881		874			883
	840(im)	857	836(im)	857	865(im)	849(im/ tbterpy)	864
					845(im)	840(im)	
					829(im)	815(im)	834
	818(im)	817	803(im)	818	805(im)		
790	781(im)	790	777(im)	788	775(im/ tbterpy)	798(im/ tbterpy)	
	766(tbterpy)	778					
	761(im)	767					
			734(im)	754	736(im)	728(im)	746
	722(im)	732	722(im/ tbterpy)	733	730(im/ tbterpy)		
			706(im)	715	724(im/ tbterpy)	708(im)	722
					707(im)		

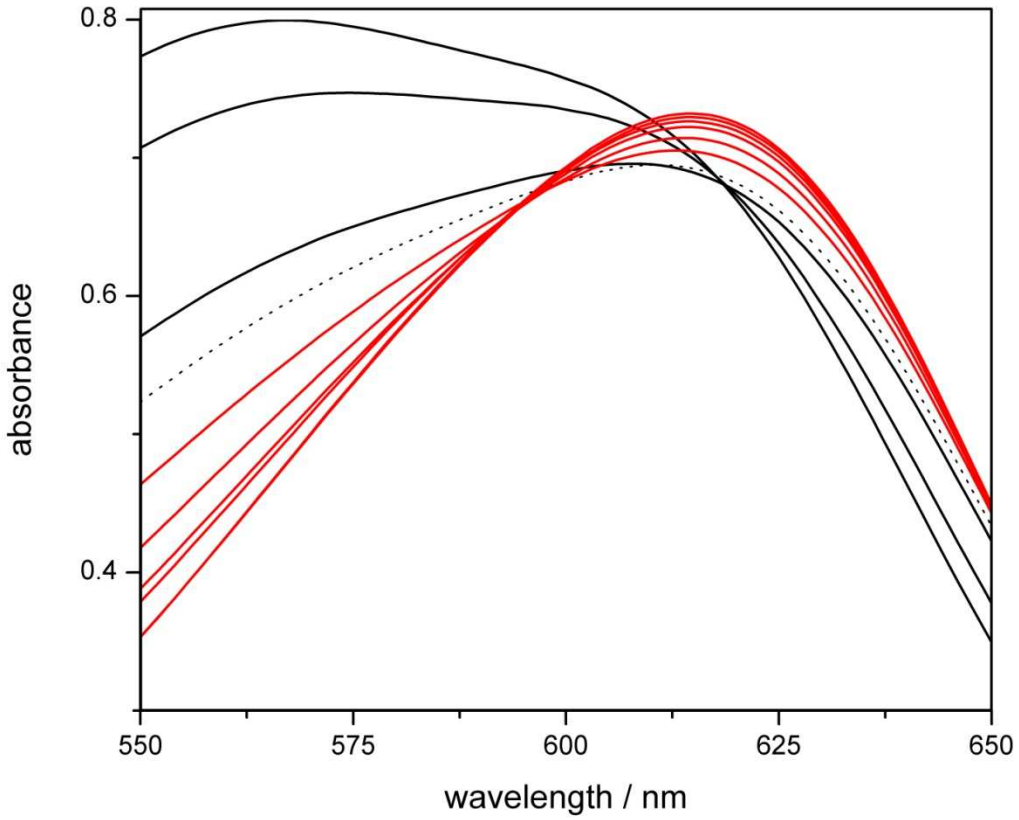


Figure S1: Example for the presence of two sets of isosbestic points upon addition of concentrated TFA in the second part of the titration; first steps isosbestic point at 618 nm, final steps at 594 nm.

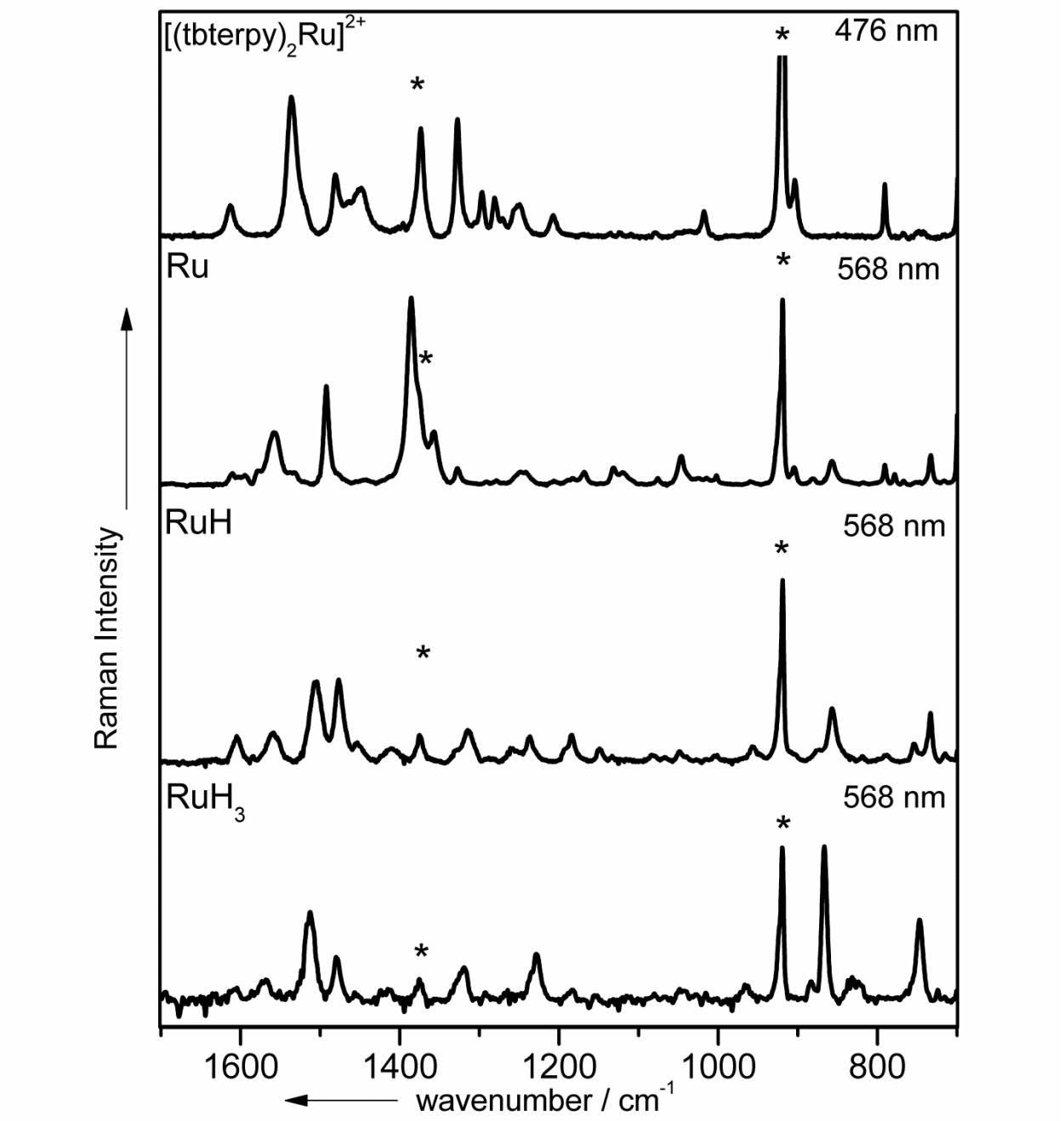


Figure S2: Experimental RR spectra of the three separately prepared protonated species in direct comparison normalized to the solvent band at 919 cm^{-1}

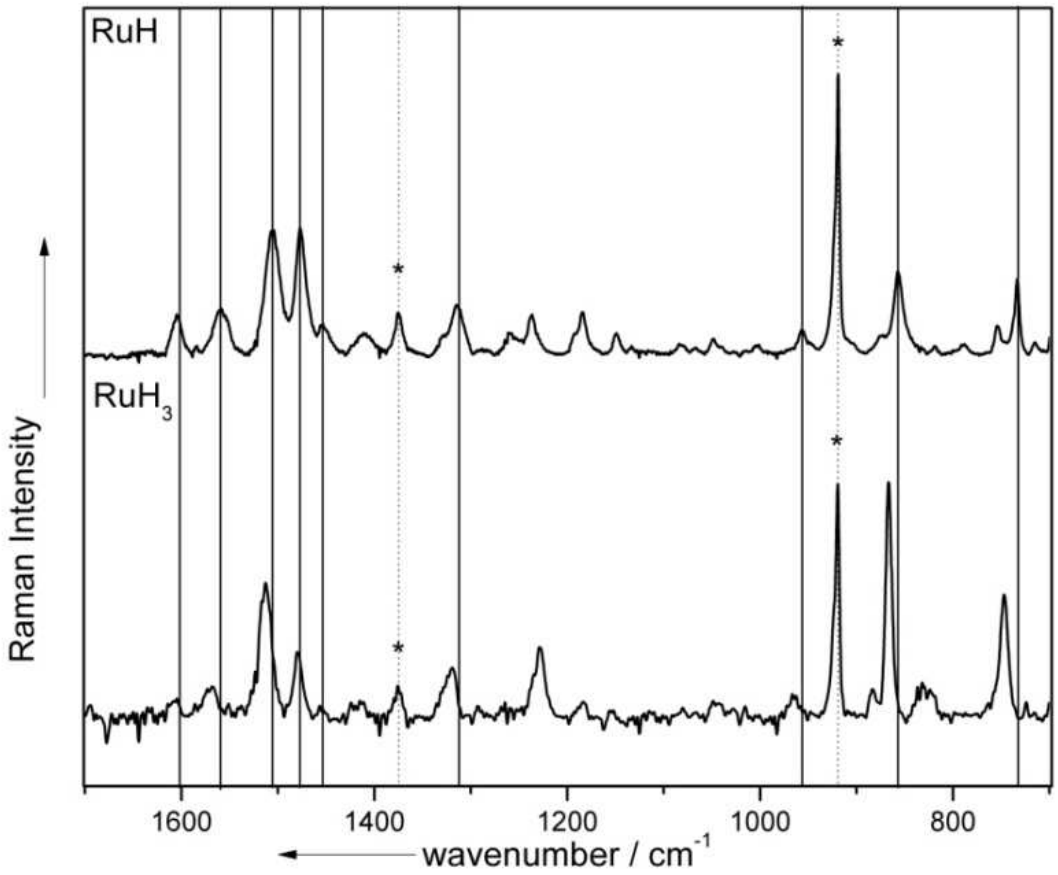


Figure S3: Experimentally observed shifts of the signal positions upon protonation of the dimethylamino groups

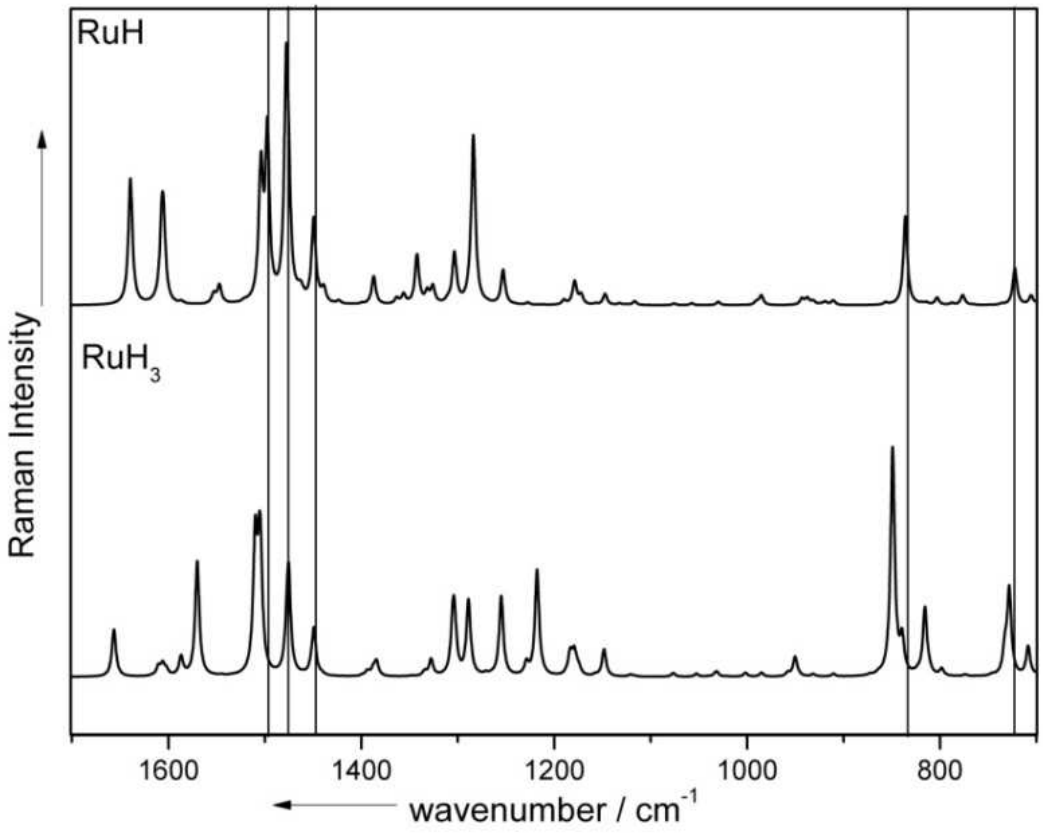


Figure S4: Calculated shifts of the signal positions upon protonation of the dimethylamino groups