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INFRARED SPECTRA OF BIPHENYL AND SEVERAL DEUTERATED BIPHENYLS

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INFRARED SPECTRA OF BIPHENYL AND SEVERAL DEUTERATED BIPHENYLS

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ABSTRACT

The infrared solution spectra of biphenyl, biphenyl-4,4'-d_2, biphenyl-2,2',6,6'-d_4, biphenyl-3,3',5,5'-d_4, biphenyl-2,2',4,4',6,6'-d_6, biphenyl-2,2',3,3',5,5',6,6'-d_8, and biphenyl-d_{10} are presented. Experimental techniques are discussed.

I. INTRODUCTION

The infrared spectra of biphenyl, biphenyl-4,4'-d_2, biphenyl-2,2',6,6'-d_4, biphenyl-3,3',5,5'-d_4, biphenyl-2,2',4,4',6,6'-d_6, biphenyl-2,2',3,3',5,5',6,6'-d_8, and biphenyl-d_{10} reported here constitute a part of a comprehensive vibrational analysis of the biphenyl molecule[1]. This investigation utilizes the infrared solution spectra, solid and liquid phase spectra, and Raman spectra. In this report the experimental infrared solution spectra only and the associated experimental techniques will be presented. The interpretation of these spectra will be presented in a subsequent paper[1].

II. EXPERIMENTAL

A. EQUIPMENT

All spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer using lithium fluoride, sodium chloride, and potassium bromide optics.

The various optical systems were calibrated with reference points from polystyrene, ammonia, atmospheric water and carbon dioxide, and mercury arc emission. When optimum calibration was obtained for each optical system a plot of error vs wavelength was made and absorption maxima were corrected accordingly. Calibration check points run with each spectrum were reproducible to ± 0.001 micron.

Wavelength assignments for absorption maxima were read from the wavelength counter to the nearest 0.005 micron for most of the peaks in the NaCl and KBr regions; in the case of broad peaks the determination of the exact point of maximum absorbance is more uncertain. In the LiF region most of the absorption maxima could be read to about 0.001 microns. These values were then corrected for calibration errors.

Spectral slit width with LiF optics varied from about 3 cm^{-1} at 1.75 microns to 1.0 cm^{-1} at 3 microns and remained constant at about 1.0 cm^{-1} from 3 to 6 microns. The spectral slit width employed with NaCl optics varied from about 2.4 cm^{-1} at 6 microns to about 1.0 cm^{-1} from 10 to 15 microns. The values for KBr optics ranged from 1.6 cm^{-1} at 16 microns to about 3 cm^{-1} at 23 microns.

Fixed thickness cells with sodium chloride or potassium bromide windows were used; cell thickness varied from 0.110 mm to 0.120 mm.

B. MATERIALS

The deuterated biphenyls used to obtain these spectra were chemically pure and none of them contained more than five molecular percent of isotopic impurity as determined by gas chromatography and mass spectrometry. Table I summarizes the analyses of these compounds. The synthesis and description of these compounds have been reported elsewhere[2]. Biphenyl was obtained from Eastman-Kodak and was purified by distillation and sublimation.

Solutions were prepared with Mallinckrodt AR carbon disulfide and Eastman Kodak Spectro Grade tetrachloroethylene. A concentration of 0.4 gram of solute per milliliter of solution was used for all spectra. Solutions were prepared as needed for each spectrum.

III. RESULTS AND DISCUSSION

The spectra are shown in Figures 1 through 7. Table II lists the absorption maxima and intensities.

The solvents, tetrachloroethylene and carbon disulfide were each used in regions where they have no strong absorption bands. In these regions the weak absorption bands of the solvent were effectively removed from the spectra by adjusting the solvent thickness in the reference beam to correspond to approximately 0.6 of the sample solution thickness. This value was established experimentally by varying the reference solvent thickness while keeping the sample solution thickness and concentration constant; the proper thickness of the reference was chosen as that which resulted in spectra free of solvent absorption bands.

Tetrachloroethylene which has no strong absorption bands below 10 microns was used as a solvent in the region from 1.5 to 8.0 microns; carbon disulfide was used from about 8.0 to 25 microns. Hence, in the LiF region tetrachloroethylene was used as the solvent; in the KBr region carbon disulfide was used. In the NaCl region tetrachloroethylene was used as the solvent from about 1.5 to 8.0 microns and carbon disulfide was used from about 8 to 15 microns.

Solvent effects were shown experimentally to be negligible[1].

Accuracy of wavelength assignments, subsequently converted to cm^{-1}, although variant, is probably better than ± 0.005 micron for all except the broad peaks and about ± 0.001 microns in the LiF region.

TABLE I

COMPOSITION OF THE DEUTERATED BIPHENYLS

Biphenyl-4,4'-d_2	$C_{12}H_8D_2$	-	97.4
	$C_{12}H_9D$	-	2.2
	$C_{12}H_{10}$	-	0.4
Biphenyl-3,3',5,5'-d_4	$C_{12}H_6D_4$	-	98.0
	$C_{12}H_7D_3$	-	1.8
	$C_{12}H_8D_2$	-	0.2
Biphenyl-2,2',6,6'-d_4	$C_{12}H_6D_4$	-	98.2
	$C_{12}H_7D_3$	-	1.6
	$C_{12}H_8D_2$	-	0.2
Biphenyl-2,2',4,4',6,6'-d_6	$C_{12}H_4D_6$	-	95.2
	$C_{12}H_5D_5$	-	4.6
	$C_{12}H_6D_4$	-	0.2
Biphenyl-2,2',3,3',5,5',6,6'-d_8	$C_{12}H_2D_8$	-	96.0
	$C_{12}H_3D_7$	-	3.8
	$C_{12}H_4D_6$	-	0.2
Biphenyl-d_{10}	$C_{12}D_{10}$	-	95.1
	$C_{12}D_9H$	-	4.7
	$C_{12}D_8H_2$	-	0.2

TABLE II

INFRARED SPECTRA OF BIPHENYL AND VARIOUS DEUTERATED BIPHENYLS

Biphenyl				Biphenyl-d_2			
cm^{-1}	Intensity*	cm^{-1}	Intensity*	cm^{-1}	Intensity*	cm^{-1}	Intensity*
5952	w	1319	w	5917	w	1397	s
4608	w	1304	w	4630	w	1375	w
4032	w	1280	w	4464	w	1355	w
3140	w	1267	m	4031	w	1332	w
3126	sh	1242	w	3102	sh	1309	w
3115	sh	1217	w	3078	s	1263	w
3106	sh	1176	w	3057	sh	1217	w
3082	s	1156	m	3035	sh	1176	w
3034	s	1107	m	3028	s	1125	w
3032	s	1074	s	3006	sh	1109	m
2976	w	1043	m	2989	w	1038	m
2924	w	1009	s	2967	sh	1008	m
2898	w	991	m	2874	w	978	m
2874	w	980	m	2481	w	963	w
2740	w	964	m	2347	w	873	sh
2667	w	917	m	2291	m	866	sh
1965	m	903	s	2281	m	858	s
1949	m	839	m	2268	m	838	s
1905	w	778	s	2237	w	763	m
1889	m	735	s	1919	m	735	m
1873	m	697	s	1887	w	719	s
1826	w	670	m	1802	w	695	m
1810	m	665	m	1773	w	653	w
1764	w	654	w	1748	w	638	w
1751	w	645	w	1724	w	609	s
1689	w	609	s	1718	w	603	sh
1667	w	544	m	1701	w	548	sh
1613	m	509	m	1686	w	535	m
1597	s	503	m	1618	w	484	sh
1571	m	493	m	1600	m	481	sh
1538	w	488	m	1591	m	479	m
1481	s	485	m	1558	m	475	sh
1458	m	483	m	1492	m	470	m
1433	s	470	m	1475	s	466	sh
1384	m	455	m	1449	m		
1337	w			1422	w		

* w - weak
m - medium
s - strong
sh - shoulder

TABLE II(continued)

Biphenyl-3,3',5,5'-d_4				Biphenyl-2,2',6,6'-d_4			
cm^{-1}	Intensity*	cm^{-1}	Intensity*	cm^{-1}	Intensity*	cm^{-1}	Intensity*
5952	w	1426	s	5917	w	1484	w
4630	w	1383	s	4630	w	1422	s
4464	w	1332	w	4464	w	1402	sh
4115	w	1250	w	4049	w	1348	m
4032	w	1183	w	4016	w	1302	m
3636	w	1104	m	3175	w	1230	w
3257	w	1093	m	3125	w	1216	w
3125	w	1073	m	3060	s	1196	w
3053	s	1048	w	3036	sh	1144	m
3016	m	999	m	3021	sh	1127	m
2998	w	977	m	2999	m	1102	m
2959	w	913	s	2865	w	1078	w
2924	w	898	s	2481	w	1010	m
2865	w	887	s	2315	w	1005	sh
2475	w	859	w	2292	w	973	m
2347	w	840	m	2269	m	922	w
2309	w	833	m	1948	m	890	m
2297	w	804	w	1900	m	879	m
2277	s	784	w	1852	w	856	w
2265	s	762	w	1812	w	834	s
2251	sh	713	sh	1792	w	817	s
2207	w	698	s	1773	w	779	s
1919	w	668	m	1761	w	764	w
1890	w	665	m	1754	m	730	s
1833	m	622	s	1745	m	700	w
1812	m	599	m	1718	w	652	w
1804	w	574	w	1709	w	628	w
1626	w	479	m	1678	w	598	s
1608	w	469	w	1650	w	549	w
1590	s	460	m	1629	w	516	m
1555	m	455	m	1592	m	474	m
1464	w	452	m	1580	m	467	m
1453	w	446	sh	1558	m	455	m
1439	w	440	m	1534	w		

* w - weak
m - medium
s - strong
sh - shoulder

TABLE II(continued)

Biphenyl-d_6				Biphenyl-d_8			
cm^{-1}	Intensity*	cm^{-1}	Intensity*	cm^{-1}	Intensity*	cm^{-1}	Intensity*
4608	w	1287	w	4468	w	1385	m
4464	w	1248	m	4000	w	1375	m
4049	w	1215	w	3788	w	1364	s
3226	w	1124	w	3247	w	1351	s
3054	s	1099	w	3115	w	1287	w
3036	sh	1078	w	3101	w	1255	w
3000	w	1009	m	3049	m	1190	w
2948	w	950	w	3012	sh	1165	w
2874	w	943	w	2959	w	1124	m
2481	w	917	s	2924	w	1095	w
2320	w	841	s	2865	w	1007	w
2309	w	831	s	2476	w	984	m
2301	w	806	m	2410	w	963	m
2278	m	792	w	2392	w	914	s
2266	m	752	s	2370	w	861	m
1950	w	740	sh	2336	w	830	m
1844	m	700	s	2317	w	817	s
1772	w	652	w	2284	s	785	w
1672	w	649	w	2261	m	720	w
1623	w	622	w	2230	w	706	w
1582	m	601	sh	1901	w	683	m
1555	w	595	m	1890	w	653	m
1541	w	574	m	1836	sh	628	s
1511	w	547	s	1831	m	597	s
1475	w	515	s	1773	w	592	s
1453	w	474	m	1610	m	546	w
1443	sh	469	m	1577	m	465	m
1433	sh	465	m	1570	m	454	sh
1420	s	460	m	1546	m	448	sh
1404	m	456	m	1475	m	444	m
1387	m	451	sh	1441	m	439	m
1375	m	446	w	1416	w	434	sh
1357	w	440	w	1401	m		
1305	w						

* w - weak
m - medium
s - strong
sh - shoulder

TABLE II(continued)

Biphenyl-d_{10}

cm^{-1}	Intensity*	cm^{-1}	Intensity*	cm^{-1}	Intensity*	cm^{-1}	Intensity*
4464	w	2075	w	1344	s	825	m
3802	w	1887	w	1328	m	815	s
3247	w	1866	w	1316	m	783	m
3225	w	1773	w	1295	w	744	m
3215	w	1754	w	1280	w	652	m
3205	w	1681	w	1263	w	625	m
2865	w	1645	w	1117	w	597	w
2481	w	1615	w	1090	w	586	s
2393	w	1605	m	1007	w	564	w
2364	w	1567	m	982	m	542	s
2315	sh	1548	w	950	m	466	m
2295	m	1529	w	912	w	455	m
2285	s	1441	m	860	m	449	sh
2280	sh	1414	w	843	m	444	m
2258	m	1401	w	835	sh	439	m
2221	w	1374	w	830	sh	434	m

* w - weak
m - medium
s - strong
sh - shoulder

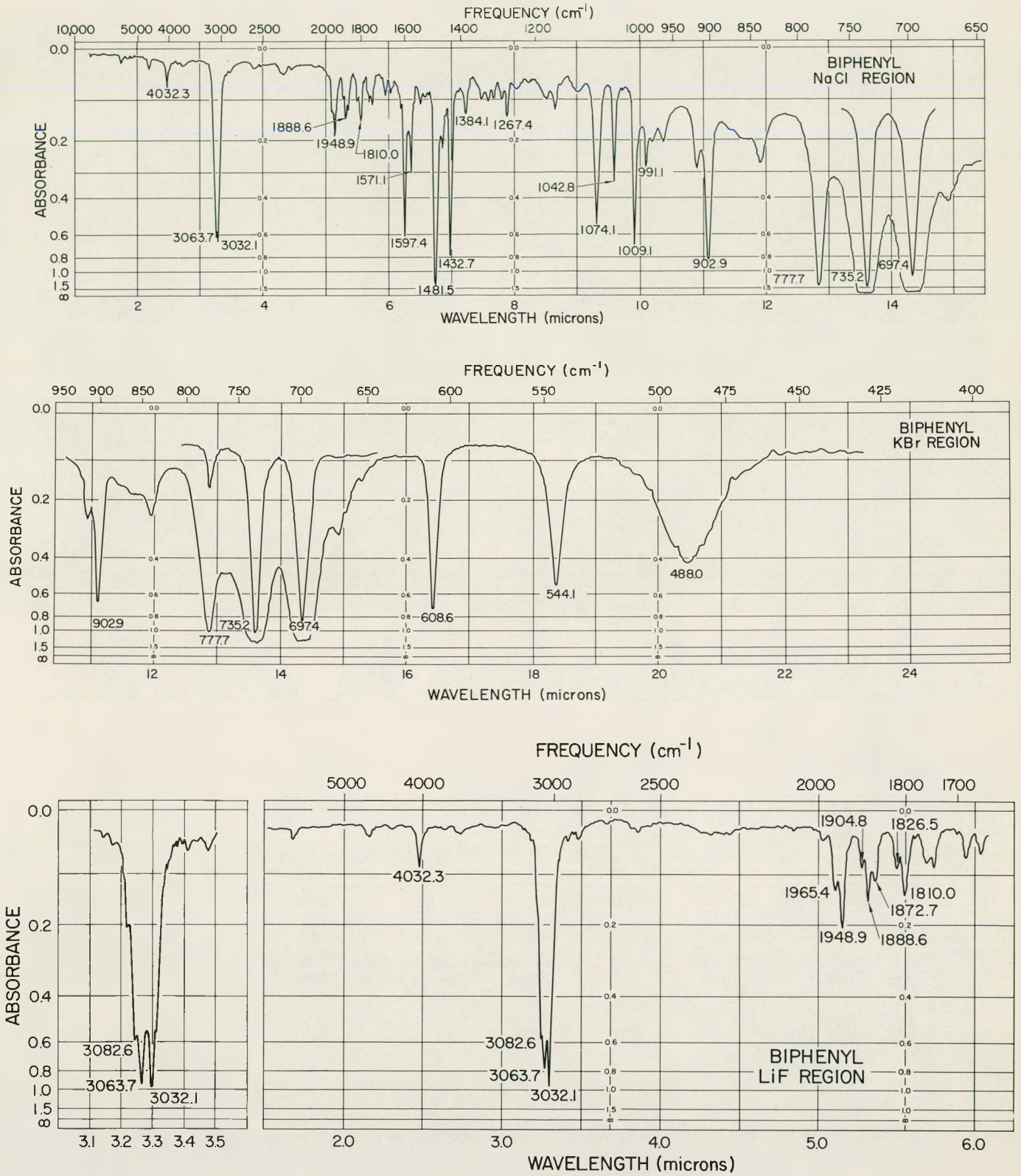

Figure 1. Spectrum of Biphenyl

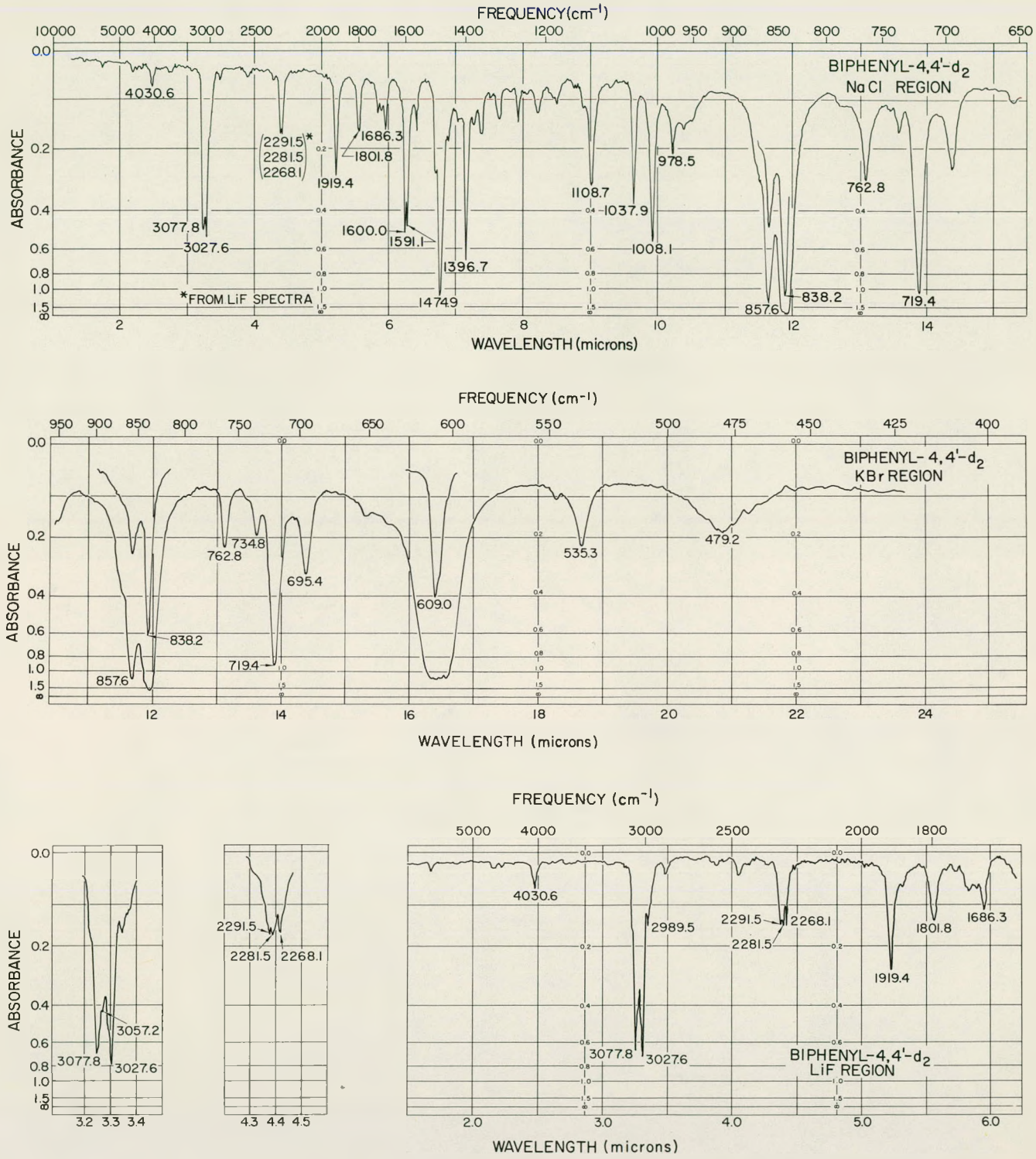

Figure 2. Spectrum of Biphenyl-4,4'-d_2

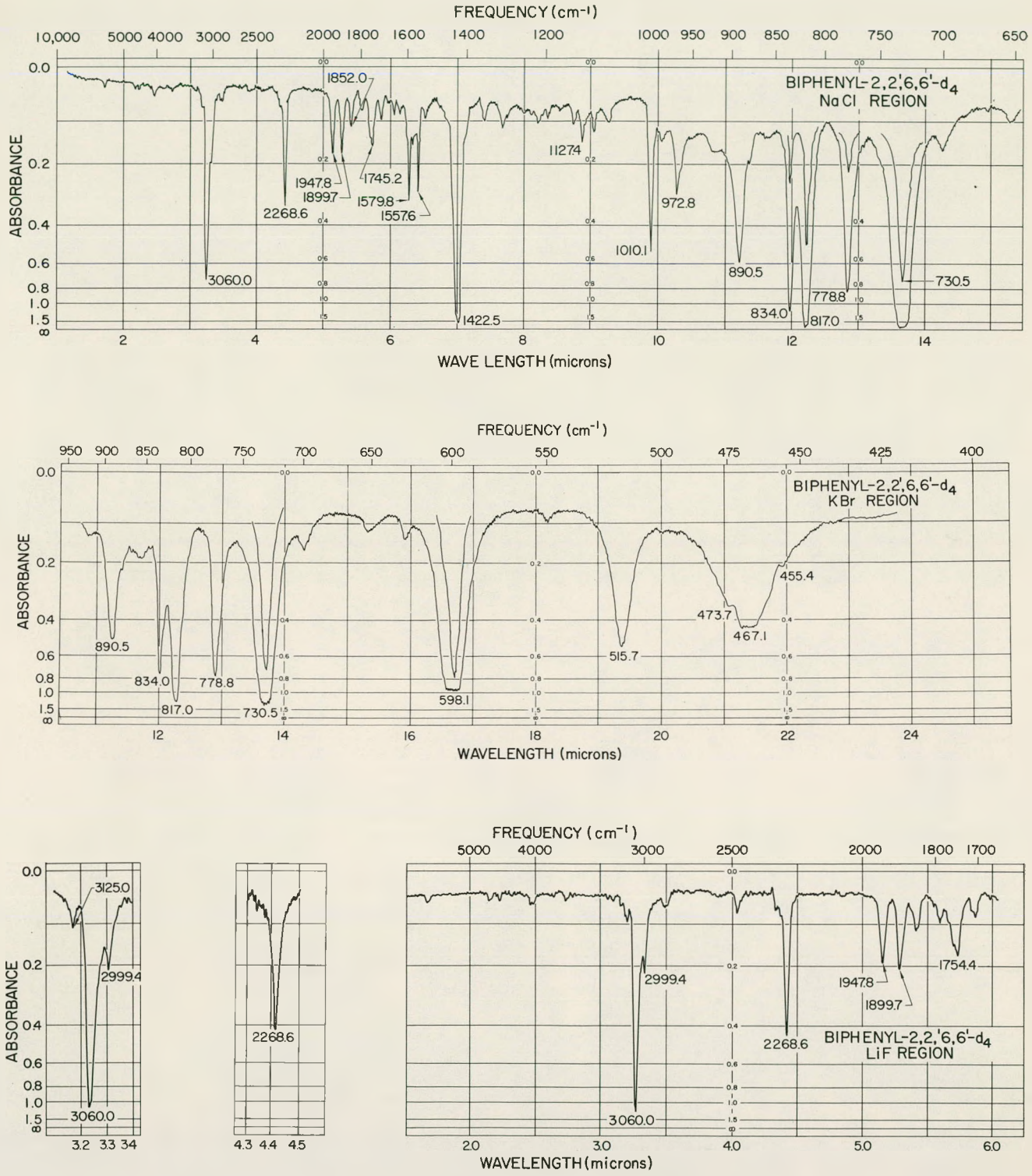

Figure 3. Spectrum of Biphenyl-2,2',6,6'-d_4

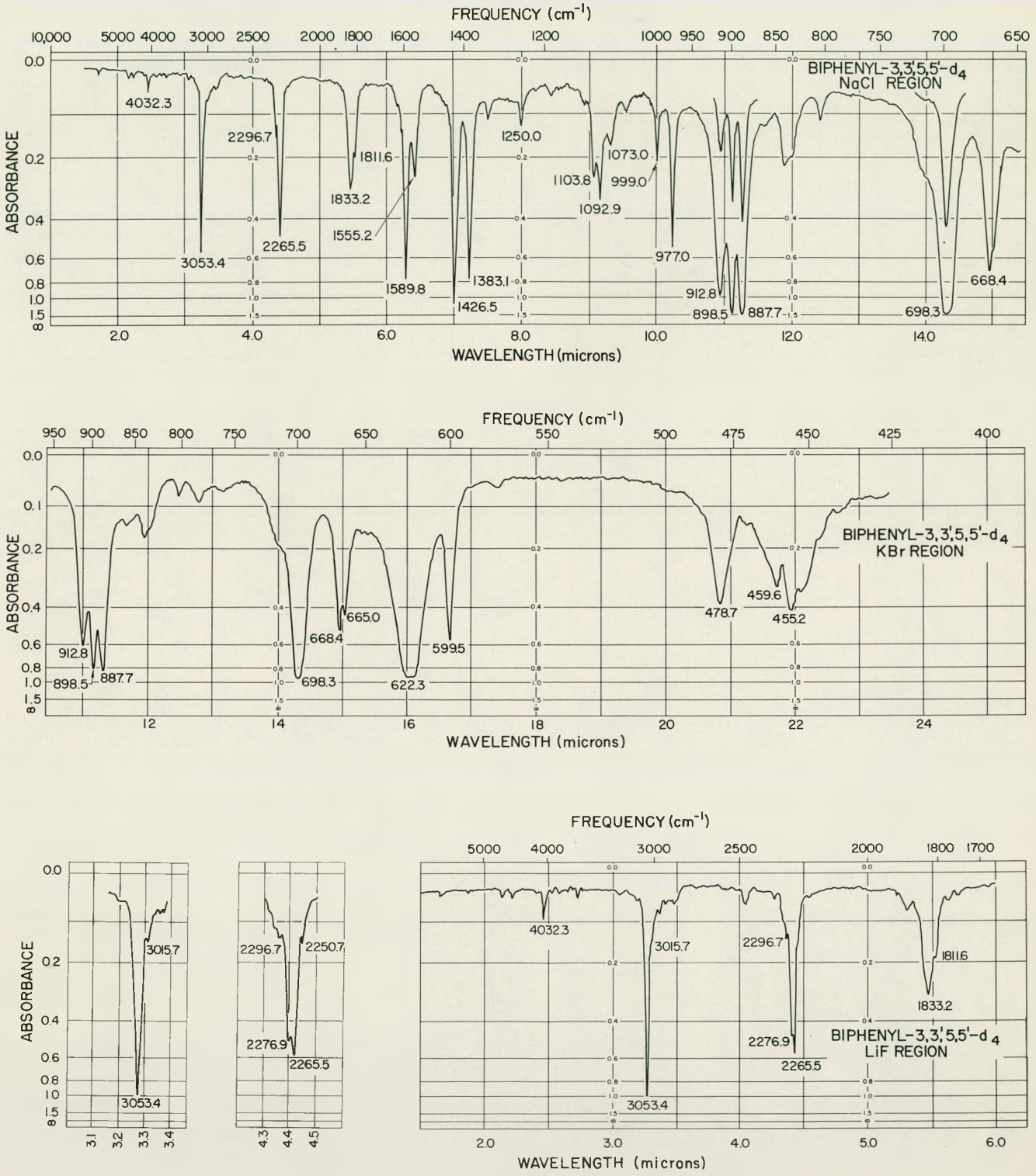

Figure 4. Spectrum of Biphenyl-3,3',5,5'-d_4

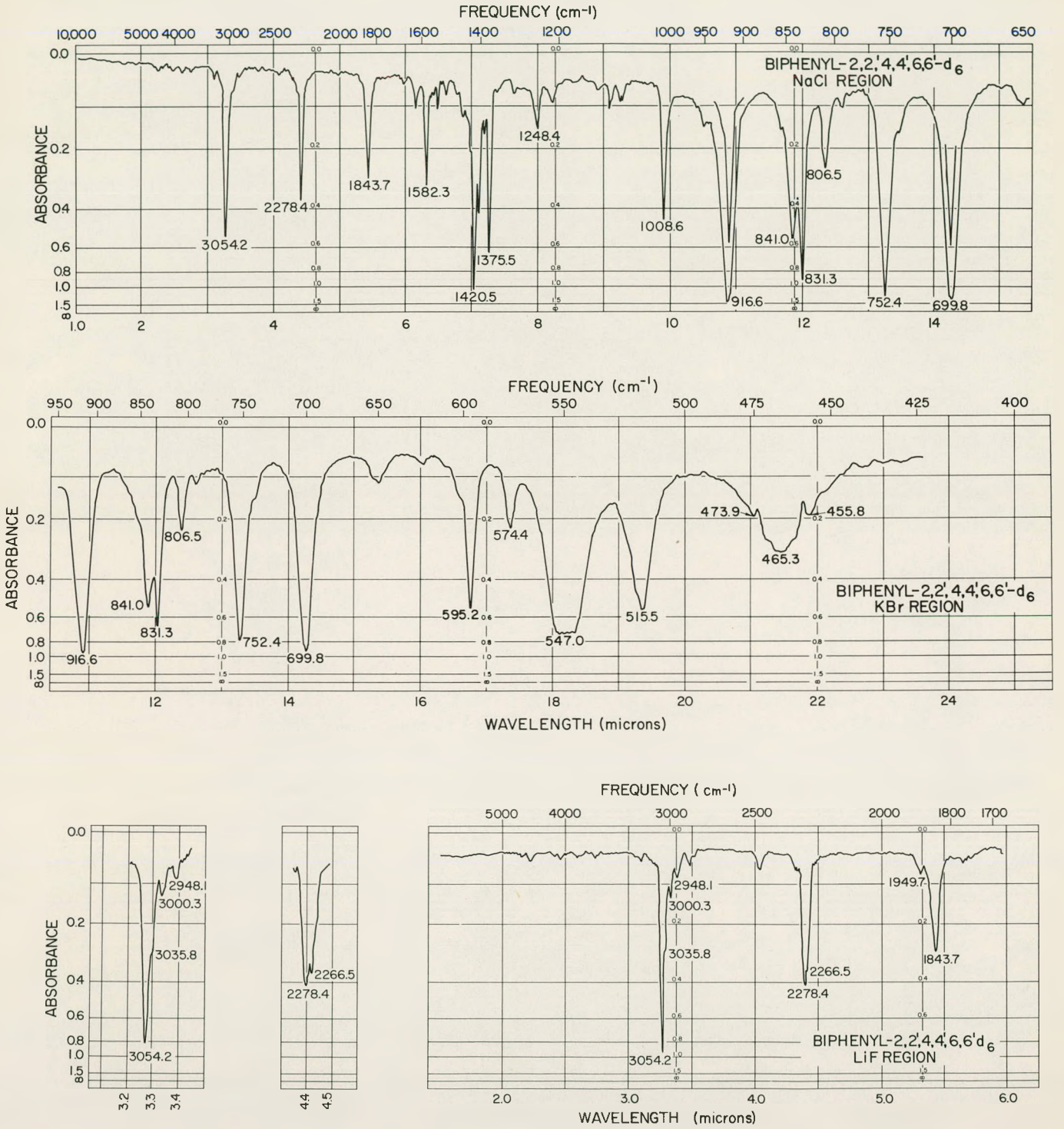

Figure 5. Spectrum of Biphenyl-2,2',3,3',5,5',6,6'-d_4

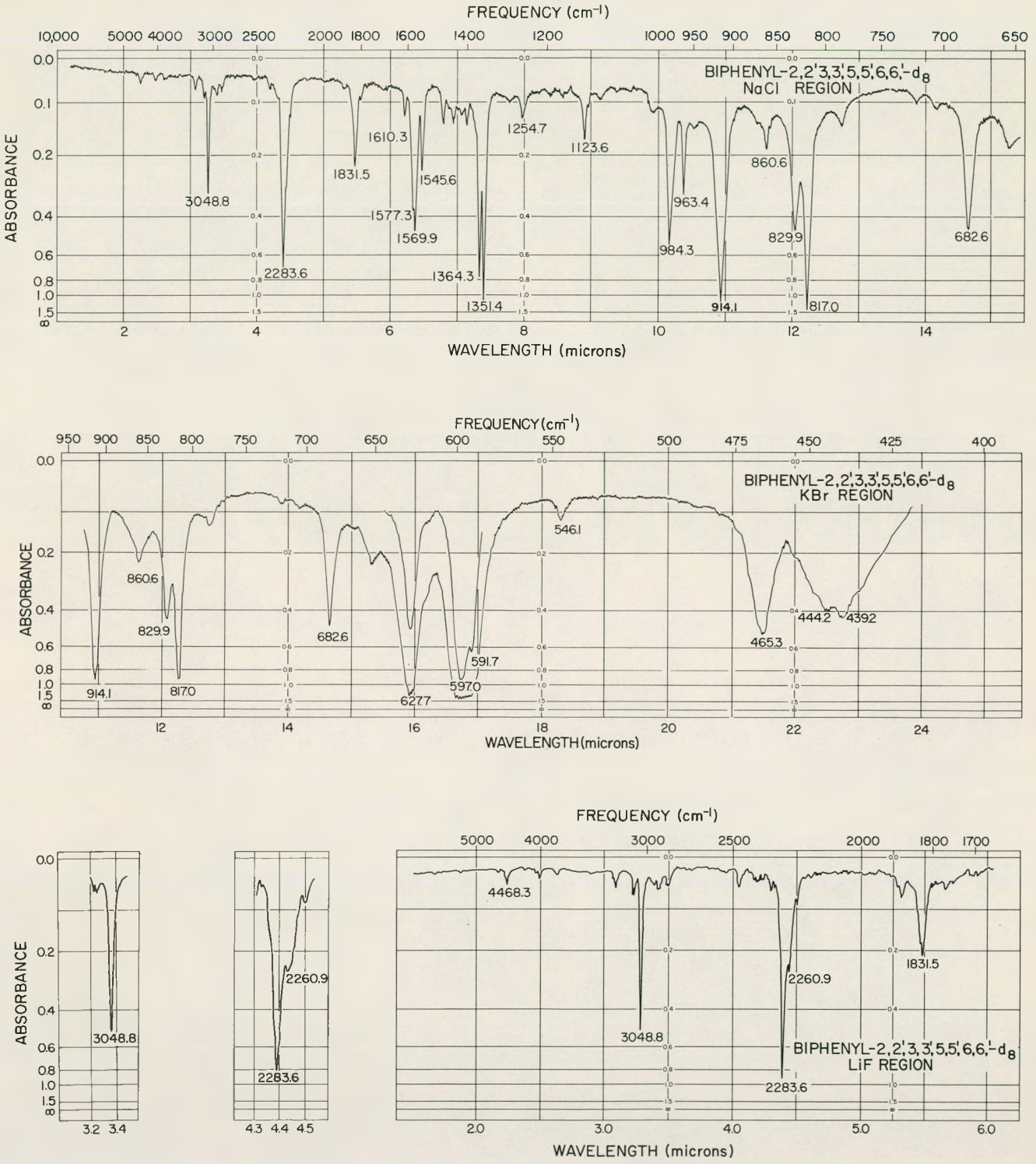

Figure 6. Spectrum of Biphenyl-2,2',5,5',6,6'-d_8

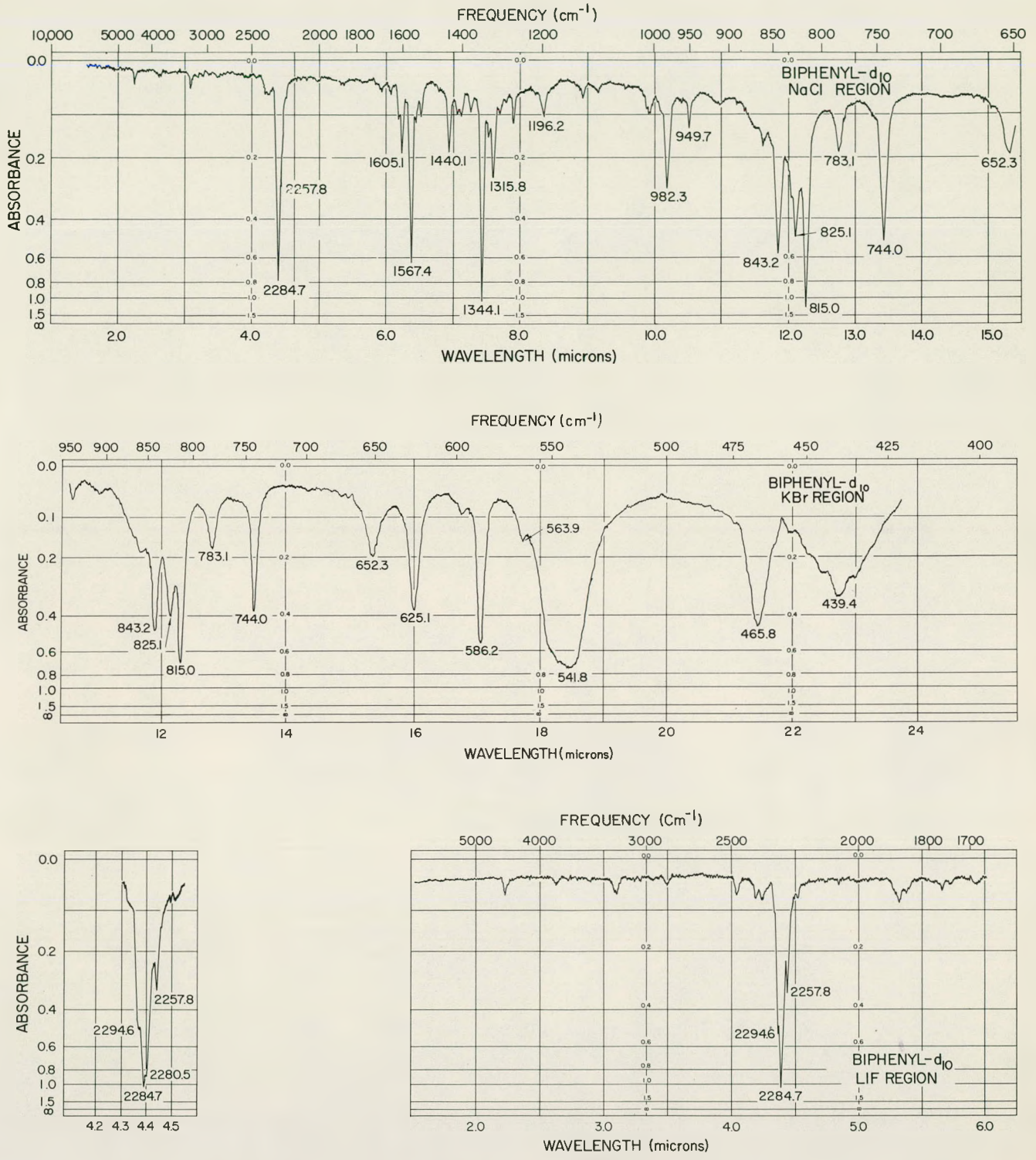

Figure 7. Spectrum of Biphenyl-d_{10}

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