The Ultraviolet Absorption Spectrum of Benzonitrile Vapor

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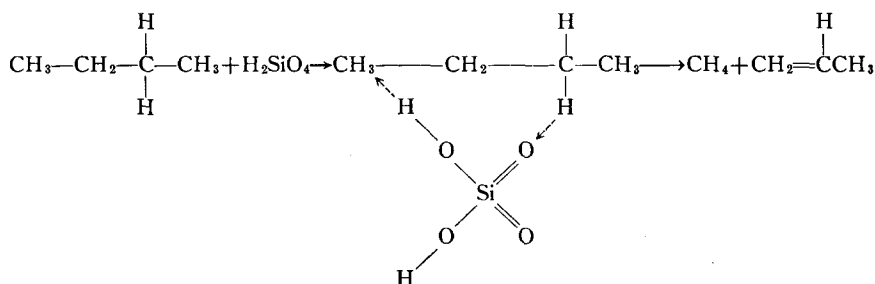
A more detailed presentation of this unitary mechanism of catalytic hydrocarbon reactions will be a subject of a subsequent communication by the senior author.

The Ultraviolet Absorption Spectrum of Benzonitrile Vapor*

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The ultraviolet absorption spectrum of benzonitrile vapor has been investigated, and many of the observed bands have been accounted for in terms of ground and excited state frequencies. The data obtained were compared with the data available from infra-red absorption spectra, the Raman effect, and early work on ultraviolet absorption spectra. The spectrum of benzonitrile vapor was shown to resemble closely the spectra of other monosubstituted benzenes, particularly in the spacing of the excited state bands from the zero-zero band.

THIS study of the ultraviolet absorption spectrum of benzonitrile vapor has the aim of extending the analyses of the spectra of monosubstituted benzenes. Since the initiation of this work, the spectra of several other monosubstituted benzenes have been reported and their main features analyzed. The present work is consistent with these analyses and allows the assignment of a large fraction of the vibrational frequencies and modes for both the ground and excited electronic states of the molecule.

The $C-C\equiv N$ grouping is known to be linear, and the symmetry class of benzonitrile should be C_{2v}. Vibrational frequencies characteristic of this grouping are known from comparison of the Raman effect and infra-red spectra of organic cyanides as well as of HCN and cyanogen. Therefore a key exists as to some of the vibrational frequencies introduced by the substituent group. Since the nitrile group possesses an unshared pair of electrons which may resonate with those in the ring, an intensification as well as a shift of the whole spectrum toward the red, as compared with that of benzene, may be expected.

Many authors have reported work on the Raman effect, infra-red, and ultraviolet spectra of benzonitrile.[1-8]

[1] J. E. Purvis, J. Chem. Soc. 107, 496 (1915).
[2] H. E. Acly, Zeits. f. physik. Chemie 135, 251 (1928).
[3] Koiti Masaki, Chem. Soc. Japan 11, 346 (1936).
[4] K. W. F. Kohlrausch, *Ramanspektren* (Edwards Brothers, Inc., Ann Arbor, 1945).
[5] J. Simons, Finska Vetenskap-Soc., Comm. Phys.-Math. 6, No. 13 (1932).
[6] J. Lecompte, J. de phys. et rad 8, 489 (1937).
[7] P. Barchewitz and M. Parodi, J. de phys. et rad. 10, 143 (1939).
[8] P. Barchewitz and M. Parodi, Comptes Rendus 209, 30 (1939).

EXPERIMENTAL

The absorption spectrum of benzonitrile vapor was photographed with a Hilger Littrow spectrograph having quartz optical parts and a dispersion of 48 wave numbers per millimeter in the region of 2740A (36,500 cm⁻¹). A hydrogen discharge tube used end-on was the light source. This tube was of the flowing type, hydrogen being introduced through a palladium thimble and pumped out by a Cenco Hyvac pump.

Absorption cells having lengths of 83 and 152 cm and quartz windows were used. The longer cell was equipped to operate as a flowing, rather than static, cell with a bulb at either end. One bulb held pure liquid benzonitrile, and the other was cooled by a dry ice-isopropyl alcohol bath. This flowing arrangement was used to avoid accumulation of decomposition products in the cell and on the cell windows.

The cells could be placed in an electrically heated furnace and the pressure controlled by the temperature of the bulb which contained the liquid.

Benzonitrile obtained from the Eastman Kodak Company was dried over calcium chloride and by passing the vapors over activated alumina. The liquid was twice distilled under reduced pressure, and introduced into the cells by vacuum distillation.

Measurement of the observed bands were made on microphotometer tracings prepared on a microphotometer-comparator nearly identical with that described by Leighton, Smith, and Henson.[9] Eastman Kodak plates of types 40, 33, and 103–0 were used both for photographing the spectra and the tracings. A drawing of the benzonitrile vapor absorption spectrum made from these tracings is shown in Fig. 1. The tracings were usually eight times the size of the original spectrum. A standard Pfund iron arc was used as a wave-length standard. The wavelengths of the observed bands were corrected to vacuum and converted into wave numbers (cm⁻¹).

The Raman effect spectrum of benzonitrile (see Table II) was photographed with a Hilger spectrograph having glass optical parts, using four H-11 mercury lamps as light sources. Measure-
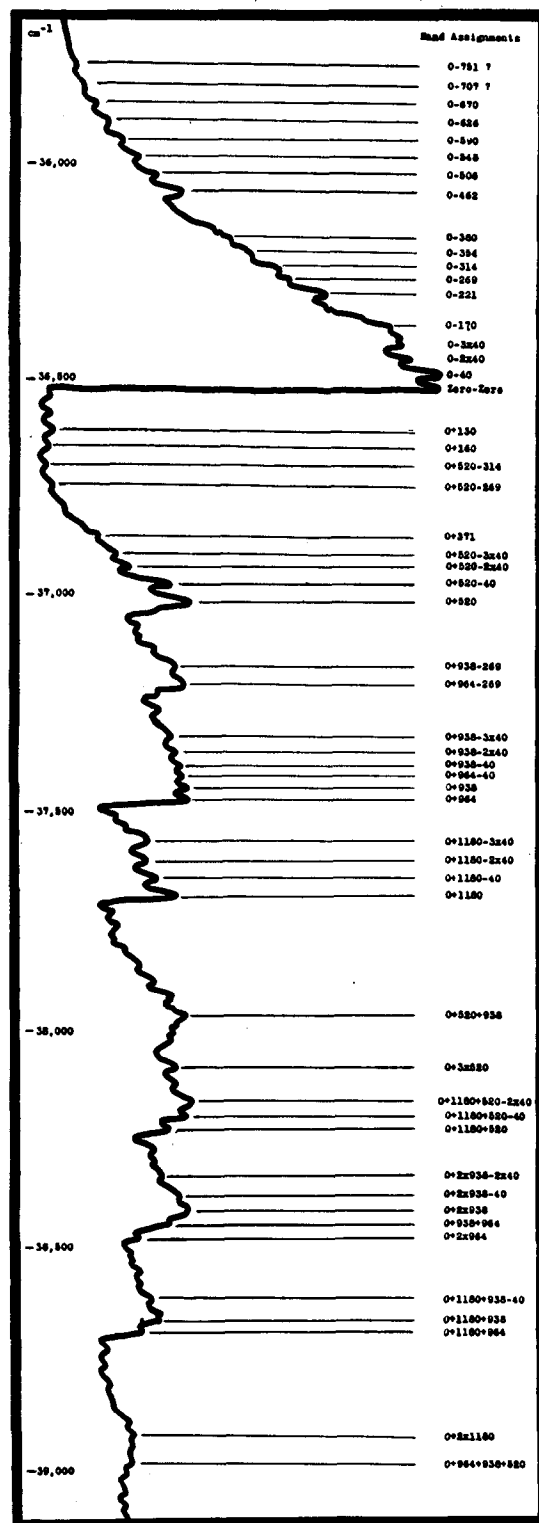
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[9] P. A. Leighton, S. Smith, and F. C. Henson, Rev. Sci. Inst. **5**, 431 (1934).

FIG. 1. Ultraviolet absorption spectrum of benzonitrile vapor (composite drawing of several microphotometer tracings).

TABLE I. Symmetry elements and selection rules for benzonitrile.

	Symmetry class	A_1	A_2	B_1	B_2
Essential	I	+	+	+	+
Symmetry	$C_2{}^y$	+	+	−	−
Elements	σ_h	+	−	+	−
	σ_v	+	−	−	+
	Translation	T_y		T_x	T_z
Selection rules	Raman effect	p	dp	dp	dp
	Infra-red	a	ia	a	a
Number of vibrations	(13 atoms)	13	3	10	7

ments were made on microphotometer tracings, and wave-lengths determined by use of a standard Pfund iron arc.[10]

THEORY

H. Sponer and E. Teller[11] have pointed out that the fundamental state of benzene has the symmetry A_{1g} and the excited state B_{2u}. The transition is then $A_{1g} \rightarrow B_{2u}$, which is forbidden in symmetry class D_{6h}. The reduction of symmetry from D_{6h} to C_{2v} by monosubstitution makes this forbidden transition into an allowed one, as Sponer and Wollman[12] have pointed out in the

TABLE II. Raman effect data on benzonitrile.

Kohlrausch* and Simons**			This research***	
Wave-number shift	Intensity	Depolar-ization (percent)	Wave-number shift	Intensity
170	8	85	170	10
381	2	35	378	3
460	6		460	6
549	5		548	5
624	5	84	623	5
751	3	15	752	4
765	5		764	6
998	15	4	1001	10
1023	3		1026	3
1178	8		1178	7
1190	8	24	1192	7
1310	1			
1353	0			
1447	1			
1493	2			
1597	10	88	1598	10
2224	10	23	2229	10
3071	8	30	3071	8
3146	1			
3196	1			

* See reference 4.
** See reference 5.
*** See reference 10.

[10] We are indebted to Dr. Robert C. Taylor of the Metcalf Research Laboratory for assistance with these Raman effect spectra. (See Table II.)
[11] H. Sponer and E. Teller, Rev. Mod. Phys. 13, 76 (1941).
[12] H. Sponer and S. Wollman, J. Chem. Phys. 9, 816 (1941).

case of monochlorobenzene. Thus the spectra of monosubstituted benzenes would be expected to show certain features of the forbidden benzene spectrum, due to the presence of the ring, together with other features of an allowed spectrum arising from the reduction in symmetry.

By analogy to the Sponer-Wollman treatment of monochlorobenzene, the electronic transition for benzonitrile is $A_1 \rightarrow B_1$, with the electronic moment lying in the plane of the ring and perpendicular to the axis of substitution. This is allowed, and should give rise to a strong band in the ultraviolet spectrum.

Table I presents the symmetry elements and selection rules for molecules of symmetry class C_{2v}. It resembles that of Sponer and Stücklen[13] for pyridine.

DISCUSSION

The most prominent feature of the ultraviolet absorption spectrum of benzonitrile vapor is the group of bands culminating in the very strong band with an extremely sharp edge on the ultraviolet side which occurs at 36,516 cm^{-1} (2737.7A). This band has been taken as the zero-zero (0→0) band. Sponer[11] and Masaki[3] also took this to be the zero-zero band.

Certain bands to the lower-wave number (red) side of the 0→0 band have been attributed to transitions from a given vibrational level of the ground state to the excited state with no vibrations active. These are shown in the "Assignments" column of Table III, and are compared to the Raman effect data, the infra-red data, and to Masaki's assignments in Table IV.

Bands at 269 and 380 cm^{-1} to the red of the 0→0 band correspond to the infra-red bands at 264 and 384 cm^{-1} reported by Barchewitz and Parodi,[7,8] and attributed by them to the nitrile group, having been found in other nitriles. Bands were found at 314, 460, 506, 548, 626, and 670 cm^{-1} to the red of the 0→0 band, and ascribed to transitions from ground state vibrational levels of these values. The 548 band is due to the ω_6'' vibration (Sponer's notation) or $6a$ (Wilson's notation).[14] The band at 626 separation is due to

[13] H. Sponer and H. Stücklen, J. Chem. Phys. 14, 101 (1946).
[14] For notation and modes of benzene ring vibrations, see K. S. Pitzer and D. W. Scott, J. Am. Chem. Soc. 65, 803–829, (1943), and E. Bright Wilson, Phys. Rev. 45, 706 (1934).

TABLE III. Observed ultraviolet bands of benzonitrile.

Wave number of band	Difference from 0→0 band	Intensity	Assignment of band
35,653	863	vf	
35,675	841	vf	0−838?
35,704	812	vf	
35,743	773	vf	0−765?
35,775	741	vf	0−751?
35,809	707	vf	
35,847	669	f	0−670
35,890	626	vw	0−626
35,926	590	vw	
35,968	548	w	0−548
36,010	506	w	0−3×170?
36,054	462	wm	0−462
36,136	380	vw	0−380
36,162	354	w	
36,202	314	wm	0−314
36,233	283	wm	
36,247	269	m	0−269
36,295	221	ms	0+160−381
36,346	170	ms	0−170
36,364	152	s	0+160−314
36,382	134	vs	0+130−269
36,397	119	vs	0−3×40
36,434	82	vs	0−2×40
36,458	58	s	
36,476	40	vvs	0−40
36,516	0	vvs	0→0
36,547	31	vw	
36,596	80	vw	
36,640	124	vw	0+130
36,676	160	vw	0+160
36,722	206	vw	0+520−314
36,767	251	vw	0+520−269
36,826	310	w	
36,887	371	w	0+371
36,922	406	wm	0+520−3×40
36,956	440	m	0+520−2×40
36,997	481	ms	0+520−40
37,036	520	ms	0+520
37,058	542	wm	
37,090	574	w	
37,114	598	w	
37,147	631	wm	
37,180	664	m	0+938−269
37,217	701	m	0+964−269
37,241	725	wm	
37,277	761	w	
37,340	824	wm	0+938−3×40
37,376	860	m	0+938−2×40
37,439	923	ms	0+964−40
37,454	938	s	0+938
37,480	964	ms	0+964
37,523	1007	w	
37,544	1028	w	
37,572	1056	wm	0+1180−3×40
37,619	1103	wm	0+1180−2×40
37,656	1140	m	0+1180−40
37,696	1180	s	0+1180
37,731	1215	vw	
37,763	1247	vw	
37,786	1270	vw	
37,811	1295	w	
37,855	1339	wm	
37,883	1367	wm	
37,916	1400	w	
37,957	1441	ms	
37,978	1462	m	0+520+938
37,993	1477	wm	
38,014	1498	wm	
38,071	1555	wm	0+3×520
38,110	1594	wm	
38,144	1628	wm	
38,176	1660	m	0+520+1180−40
38,207	1691	wm	0+520+1180
38,252	1736	vw	
38,277	1761	vw	
38,310	1794	w	0+2×938−2×40
38,358	1842	wm	0+2×938−40
38,377	1861	wm	
38,393	1877	ms	0+2×938
38,416	1900	m	0+938+964
38,448	1932	w	0+2×964
38,497	1981	f	0+2×520+938?
38,525	2009	vw	0+2×520+964?

TABLE III.—*Continued.*

Wave number of band	Difference from 0→0 band	Intensity	Assignment of band
38,588	2072	wm	0+938+1180−40
38,620	2104	wm	
38,632	2116	m	0+938+1180
38,653	2137	m	0+964+1180
38,696	2180	f	
38,768	2252	f	
38,854	2338	f	
38,881	2365	vw	0+2×1180
38,905	2389	f	
38,936	2420	f	0+520+938+964
38,960	2444	vw	0+520+2×964
39,008	2492	vw	0+130+2×1180?
39,042	2526	vw	
39,096	2580	w	
39,121	2605	w	
39,149	2633	vw	0+520+938+1180?
39,192	2676	vw	
39,209	2693	vw	
39,224	2708	f	
39,265	2749	f	
39,287	2771	f	
39,325	2809	f	
39,340	2824	vw	0+3×938
39,363	2847	vw	0+2×938+964?
39,397	2881	f	0+520+2×1180?
39,418	2902	f	0+3×964
39,442	2926	f	
39,490	2974	f	0+2×520+2×964?
39,558	3042	f	
39,570	3054	f	0+2×938+1180?
39,597	3081	f	0+938+964+1180
39,629	3113	f	0+2×964+1180?
39,641	3125	f	
39,655	3149	f	
39,728	3212	f	
39,746	3230	f	
39,772	3256	f	
39,795	3279	f	
39,809	3293	f	0+938+2×1180?
39,818	3302	f	
39,834	3318	f	0+964+2×1180?
39,849	3333	f	0+520+3×938?
39,864	3349	vf	
39,939	3423	f	
39,947	3431	f	
39,972	3456	f	
40,006	3490	vf	
40,038	3522	f	0+3×1180
40,084	3568	f	
40,111	3595	f	
40,142	3626	f	
40,176	3660	vf	
40,183	3667	vf	
40,219	3703	f	
40,251	3735	f	
40,261	3745	f	
40,270	3754	vf	0+4×938?
40,287	3771	vf	
40,312	3796	f	
40,325	3809	vf	0+2×938+2×964?
40,358	3842	f	
40,382	3866	f	0+4×964?
40,412	3896	f	
40,484	3968	f	
40,533	4017	f	
40,559	4043	f	
40,592	4076	f	
40,626	4110	f	
40,648	4132	f	
40,662	4146	f	
40,701	4185	f	
40,731	4215	f	
40,777	4261	f	
40,860	4344	vf	
40,977	4461	f	
41,177	4661	f	
41,263	4747	f	0+4×1180?
41,340	4826	vf	
41,413	4897	vf	
41,466	4950	vf	
41,485	4969	vf	
41,509	4993	vf	
41,521	5005	vf	
41,533	5017	vf	

the ring frequency ω_4'' (or 6b). Both the 6a and 6b vibrations have the value of 606 in benzene, but split in the monosubstituted benzenes.

Measurements at higher temperatures and pressures indicate that there is still some absorp-

TABLE IV. Comparison of ground state frequencies obtained from Raman effect, infra-red, and ultraviolet spectra data on benzonitrile.

| Infra-red | | Raman effect | | Ultraviolet | |
Barchewitz and Parodi[*][**]	Lecompte[***]	Kohlrausch[†]	This research[††]	Masaki[†††]	This research
—	—	170	170	—	170
206	—	—	—	—	—
264	—	—	—	—	269
323	—	—	—	—	314
384	—	381	378	—	380
—	—	460	460	459	462
—	548	549	548	547	548
—	616	624	623	616	626
—	676	—	—	—	670
—	686	—	—	—	—
—	754	751	752	—	741
—	—	765	764	—	773
—	838	—	—	—	841
—	922	—	—	—	—
—	1002	998	1001	1009	—

[*] See reference 7.
[**] See reference 8.
[***] See reference 6.
[†] See reference 4.
[††] See reference 10.
[†††] See reference 3.

tion below 35,846 cm^{-1}, but the identification of the individual bands is uncertain because of the diffuseness and low intensities. Diffuse bands were found at separations from the 0→0 band of 707, 741, 773, 812, 841, and 863 cm^{-1}. The symmetric ring "breathing" frequency, ω_1'', could not be identified even on plates made with the highest pressures, though Masaki reported a band at 1009 cm^{-1} separation.

A very strong band is found at 40 cm^{-1} from the 0→0 band. This has been ascribed to a difference frequency which occurs between a ground state vibration and that same vibration in the excited state, that is, a so-called 1→1 type of transition. It is closely analogous to the 60 cm^{-1} difference that is so prominent in the spectrum of monochlorobenzene[12] and to the 59 cm^{-1} difference in toluene.[15] The lowest frequency found in the Raman effect is 170 cm^{-1}. This is a strong band, with an intensity of 8, and is 85 percent depolarized. A relatively strong anti-Stokes line of this frequency was observed by us[10] with only a 3-hr. exposure. It would seem preferable to correlate this 40-difference frequency with the lowest frequency of vibration of the molecule, for it must arise from a vibrational frequency having a high Boltzmann factor to appear so strongly

and so often as a difference frequency in the ultraviolet spectrum.

A medium-strong band was found 170 cm^{-1} to the red of the 0→0, as a shoulder on a stronger group of bands. A band which corresponds to the upper state frequency of this vibration would be expected at a separation of 170−40=130 to the ultraviolet of the 0→0 band. A weak, though quite distinct, band is found at a value of 124 cm^{-1} above the 0→0.

This ground state frequency of 170 cm^{-1} is believed to be that of the bending of the nitrile "tail" of the molecule out of the plane of the ring, i.e., as a "warping" of the most distant atoms of the molecule out of the plane of the ring. This motion would belong to a B_2 symmetry. According to Table I, this frequency should appear depolarized in the Raman effect. This it does, with a depolarization of 85 percent.

Vibrations of class B_2 should be active in infra-red absorption. The data of Barchewitz and Parodi, unfortunately, only extend as low as 180 cm^{-1}, so the question of the presence of an infra-red band at or near 170 cm^{-1} must go unanswered.

This difference frequency of 40 appears quite often in the ultraviolet spectrum, and also its multiples of 2×40 and 3×40. Each major upper state band has its train of 40, 2×40, and 3×40 bands to the red. It should be noted that these multiples are actually 2×130−2×170 and 3×130−3×170.

The first major band to the ultraviolet side of the 0→0 band occurs at 37,036 cm^{-1}, or 520 distant. This is assigned to an upper state vibrational frequency of 520. This would be the ω_6', or 6b, vibration. This is a characteristic frequency of the benzene ring and is not appreciably changed by the nature of the monosubstituted group. F. A. Matsen[16] showed that a number of monosubstituted benzenes had this upper state frequency between 505 and 528 cm^{-1}.

At separations of 938 and 964 cm^{-1} from the 0→0 band, two very strong bands were found, with weaker bands to their red sides. The stronger band at 938 is assigned to the ω_1', or 1, symmetric ring "breathing" frequency. The 964 band is assigned to the ω_2', or 18a, mode of vibration.

[15] N. Ginsburg and F. A. Matsen, J. Chem. Phys. 14, 511 (1946).

[16] F. A. Matsen, talk before the Symposium on Color and Electronic Spectra of Complex Molecules, Chicago, Illinois, December 30, 1946, and F. A. Matsen, W. W. Robertson, and R. L. Chuoke, Chem. Rev. 41, 273 (1947).

Bands of the 40-difference frequency and its multiples were found to the red of the 938 band, but the weaker corresponding band for the 964 were obscured by those of the 938.

A strong band at 1180 separation is assigned to the upper state frequency of the 7a vibration. This was the highest wave number band having the very sharp ultraviolet edge. The 40-multiple series was very prominent to the red of this band.

The stronger bands observed appeared to have a doublet nature. However, the resolving power of the spectrograph and plates used was not sufficient to permit full resolution of these doublets. The width of the bands measured 2.4 cm^{-1}, which corresponds to the value of 2.7 cm^{-1} earlier reported by Acly.[2] The granularity of the plates used was sufficient to impair the accuracy of these measurements.

A prominent band appears at 231 cm^{-1} to the red of the 0→0 band. It cannot be accounted for in terms of a ground state frequency, and it appears feasible to assign it to a difference frequency arising from a 1→1 transition from 381 to 160 cm^{-1}. A weak, though prominent, band occurs at 160 cm^{-1} to the ultraviolet of the 0→0, and a band at 381 cm^{-1} to the red, which corresponds to a value of 384 in infra-red absorption and 381 in the Raman effect, 36 percent depolarized. This is ascribed to a mode of vibration similar to that of 16a in benzene, with the nitrile group bending out of the plane of the ring, and the ring proper describing a "buckling" motion. This mode would have twice the number of nodes of that causing the 40-cm^{-1} difference, and it is noted that 381 is very roughly twice 170, in comparing the ground state frequencies.

Both these modes of vibration from which arise the difference frequencies of 40 and 221 belong to class B_2. B_2→B_2 transitions are allowed, and should appear strongly, as they are found to do. However, examination of the selection rules shows that transitions from a non-vibrating ground state, A_1, to a B_2 vibrating upper state should not occur, nor should B_2→A_1. Weak bands are observed, however, to which it is convenient to make such assignments. The distortions from the C_{2v} symmetry caused by the participation of the nitrile "tail" of the molecule in the vibrations of

the molecule probably make such transitions possible, with low intensities.

Progressions and combinations of the totally symmetric A_1 frequencies are allowed, and appear prominently in the ultraviolet spectrum. This is noticeable in Table III and Fig. 1. The bands farther toward the ultraviolet become increasingly complicated and less distinct because of these combinations and dissociation. Above 40,000 cm^{-1} the bands are indistinct, although some bands were observed as high as 41,533 cm^{-1}. Assignments of these higher wave number bands are necessarily uncertain, however well the assignment may fit.

The benzonitrile molecule, having an unshared pair of electrons on its substituent group, should have its 0→0 band displaced toward higher wavelengths from the theoretical position of the 0→0 band of benzene, like other molecules whose substituent groups may contribute to resonance with the ring. It occurs at 36,516 cm^{-1}, near those of bromobenzene (36,997) and phenol (36,349).

A comparison of the upper state vibrational frequencies with those of other monosubstituted benzenes is shown in Table V.

TABLE V. Comparison of excited (upper) state frequencies for various monosubstituted benzenes.

Molecule	Excited state frequencies							Reference
(Wilson notation)	—	6a	6b	12	1	18a	7a	14
Benzonitrile	371	—	520	—	938	964	1180	this work
Chlorobenzene	372	—	521	—	931	966	1190	12
Bromobenzene	—	—	518	—	931	962	1208	a
Fluorobenzene	332	410	517	779	915	966	1218	b
Toluene	—	—	527	—	930	964	1189	c
Phenol	374	476	562	783	935	975	1273	d
Deuterophenol	—	471	550	772	933	959	1268	d
Aniline	338	492	567	797	953	984	1184	d
Deuteroaniline	—	481	563	787	953	964	—	d
Methylaniline	—	442	550	775	954	973	—	d
D-methylaniline	—	426	544	780	953	965	—	d
Anisol	—	—	527	759	934	954	1270	d
Ethylbenzene	—	—	527	—	940	—	1235	16
N-propylbenzene	339	—	527	—	949	—	1258	16
Isopropylbenzene	353	—	516	—	944	—	1234	16
N-butylbenzene	366	—	540	—	949	—	1273	16
S-butylbenzene	343	—	505	—	946	—	1229	16
T-butylbenzene	333	—	510	—	955	—	1290	16
Phenyl-cyclo-hexane	318	—	523	—	934	—	1184	16

a K. Asagoe and Y. Ikemoto, Phys.-Math. Soc. Japan 22, 677 (1940).
b S. H. Wollman, J. Chem. Phys. 14, 123 (1946).
c N. Ginsburg, W. W. Robertson, and F. A. Matsen, J. Chem. Phys. 14, 511 (1946).
d N. Ginsburg and F. A. Matsen, paper presented before the Symposium on Color and Electronic Spectra of Complex Molecules, Chicago, Illinois, December 30, 1946.