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Absorption Spectrum of the 2000 Å System of Borazine in the Gas Phase*

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The optical absorption spectrum of borazine vapor, at pressures between 0.1 and 5 mm Hg, has been obtained in the wavelength region 2015 Å–1800 Å on a 2.0 m vacuum spectrograph both photoelectrically and photographically. On the basis of vibronic analysis, observed absorption features are consistent with a single π–π^*, dipole-forbidden, electronic transition, $^1A_1' \leftarrow {}^1A_1'$, assuming the D_{3h} point group is a valid description for both ground and excited electronic states of borazine. Absorption and emission to the red of this state have been searched for but neither have been observed under current sensitivity conditions. It is concluded that the excited $^1A_1'$ state is most likely the lowest singlet excited state of borazine. This spectrum is discussed in comparison with that of benzene; the $^1A_1'(D_{3h})$ state of borazine corresponds to the $^1B_{1u}(D_{6h})$ state of benzene. In particular, the $^3B_{1u} \leftarrow {}^1A_{1g}$ spectrum is compared to the $^1A_1' \leftarrow {}^1A_1'$ absorption. Arguments are presented suggesting the Jahn–Teller nature of the $^1A_1'$ excited state of borazine. In this framework, various possible excited state vibrational assignments are presented.

I. INTRODUCTION

Borazine, $B_3N_3H_6$, is an extremely interesting chemical species which has received relatively little attention since its synthesis by Stock and co-workers in 1926.[1] Since this time it has been thought of as "inorganic benzene." The two compounds are isoelectronic, planar, and one can easily picture six π-electrons contributed by three nitrogen atoms delocalized around a planar ring to form an "aromatic system." General physical properties of benzene and borazine are surprisingly similar.[1] Even though it is possible to visualize more "valence bond" or "resonance" structures, especially of a localized nature, for borazine than benzene, their average bond lengths and π-electron ionization potentials are virtually identical. Recent electron diffraction data are not inconsistent with a lower symmetry than a D_{3h} planar structure,[2] but no compelling evidence of a spectroscopic nature has been presented to strengthen and support this possibility.

In light of these parallels between benzene and borazine, a statement on details of their electronic and geometrical structure, both in the gas phase and single crystal, would certainly be of general interest. Such a large amount of optical spectroscopy is available for benzene vapor[3] and crystal[4] and so little for borazine that it was felt a study of borazine optical absorption and emission spectra should be undertaken. The main thrust of this investigation is the spectrum of single crystal borazine, whose structure is purported to be isomorphous to that of benzene.[5] A comparison of intermolecular interactions in two such similar systems will prove interesting and informative. A preliminary to this investigation (which is currently underway in our laboratory) is the gas phase spectrum of borazine which is presented here.

II. THEORETICAL PREDICTIONS OF ELECTRONIC STATES AND ENERGIES

A theoretical treatment of the energy levels of borazine parallels quite closely the theoretical description for benzene. If one labels ring atoms of borazine a through f, starting with the B atom at 12 o'clock in Fig. 1 and proceeding around the ring clockwise, the following zero order π-molecular orbitals composed from $2p_z$ orbitals of boron and nitrogen obtain

$$\left.\begin{aligned}\Psi_1&=(6)^{-1/2}[\phi_a+\phi_b+\phi_c+\phi_d+\phi_e+\phi_f]\\ \Psi_2&=(6)^{-1/2}[\phi_a-\phi_b+\phi_c-\phi_d+\phi_e-\phi_f]\end{aligned}\right\} A_2''$$

$$\left.\begin{aligned}\Psi_3&=(12)^{-1/2}[2\phi_a+2\phi_b-\phi_c-\phi_d-\phi_e-\phi_f]\\ \Psi_4&=\tfrac{1}{2}[\phi_c-\phi_d-\phi_e+\phi_f]\\ \Psi_5&=(12)^{-1/2}[2\phi_a-2\phi_b-\phi_c+\phi_d-\phi_e+\phi_f]\\ \Psi_6&=\tfrac{1}{2}[\phi_c+\phi_d-\phi_e-\phi_f].\end{aligned}\right\} E'' \qquad (1)$$

In terms of D_{6h} irreducible representations, these states transform in the following manner: $\Psi_1(A_{2u})$, $\Psi_2(B_{2g})$, $[\Psi_3, \Psi_4]$ (E_{2u}), $[\Psi_5, \Psi_6]$ (E_{1g}). A complete correlation diagram for $D_{6h} \leftrightarrow D_{3h}$, uniquely defining axis choice, is given in Fig. 2. A secular determinant can then be written of a form quite similar to that for benzene. This approach is well outlined in the literature. Integrals, as well as the form of the Hamiltonian $\mathcal{H}$ for a planar aromatic system, are discussed in detail.[6] It is then possible to produce an orbital diagram identical to that of benzene, giving rise to $(\pi$–$\pi^*)$ configurations A_1', A_2', E', for the "first excited states" of this D_{3h} orbital picture. As in benzene, the A_1', A_2', E' degenerate manifold splits into three "first excited states" for singlets and triplets under inclusion of interelectronic repulsion. It should be noted that this simple orbital picture still results if the added complication of different Coulomb integrals for boron and nitrogen atoms is introduced, and thus borazine remains an "alternant hydrocarbon." Several researchers have, over the past 25 years, attempted to calculate energies for these excited states; their results differ considerably and are shown in Table I.

It is quite clear that theoretical work on borazine

is far less definitive than that on benzene. Theoretical ordering of states in borazine seems to be open to question; calculations are very approximate partly due to a lack of semiempirical parameters for B–N systems. The original work by Roothaan and Mulliken[7] on borazine was quite approximate in nature and strongly based on an assumed one-to-one correlation between benzene and borazine. Their semiempirical Hückel-type calculation was a departure from previous thinking about borazine in that π-electrons were assumed to move in a potential derived from neutral boron and nitrogen atoms.

A number of more modern calculations (Table I) have been published,[8,9] embodying improved techniques of Pariser–Parr, Pople–SCF, and LCAO–MO–SCF schemes.[6] The most complete and systematic seems to be that of Chalvet, Daudel, and Kaufman.[8] They compare three methods, a semiempirical Hückel approach, a Pariser–Parr approximation, and a Pople–SCF calculation, for different "starting models," all of which give rise to the same energy level ordering.

More recently, an *ab initio* SCF–MO and CI calculation comparing borazine and benzene has appeared.[9] While results of this work are not as promising as those of Ref. 8, some interesting conclusions can be reached from them. First, as with the semiempirical schemes of Ref. 8, proper orbital ordering for borazine (same as that for benzene)[10] is obtained. Second, σ–π^* transitions are of low energy (about 0.5 eV above highest

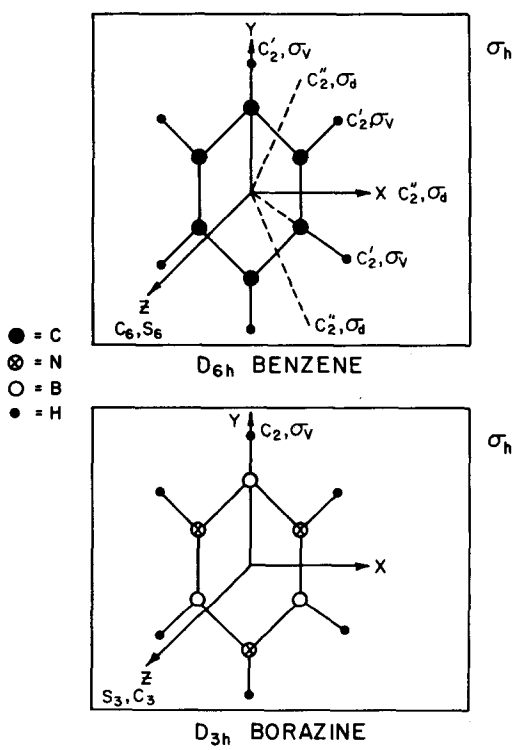

FIG. 1. Coordinate system and point group operations for benzene and borazine.

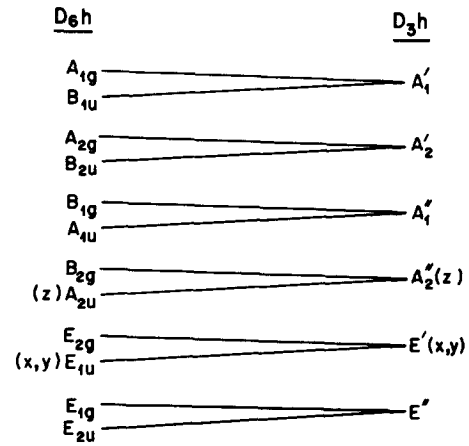

FIG. 2. Correlation table for mapping of point group D_{6h} into D_{3h}, $C_2'(Y)$ axis preserved. x, y, z transform as indicated in the two groups. (See Fig. 1.)

π–π^* transition) and double and triple excitations are considered important.

It seems clear that there is general disagreement among the various calculations even as to the order of energy levels. All one can say is that such calculations as found in Ref. 8 and perhaps Ref. 9, which give reasonable results for benzene and heterocycles, may well be of value for borazine.

III. EXPERIMENTAL TECHNIQUES

A. Synthesis and Sample Preparation

The method used to synthesize borazine was that described by Schaeffer *et al.*[11] involving solid reactants in the absence of a solvent. The over-all reaction is probably quite complex but can be schematically represented as,

$$3LiBH_4+3NH_4Cl\rightarrow B_3N_3H_6+3LiCl+9H_2.$$

Figure 3 is a diagram of the vacuum system used to carry out this synthesis. Initially it was assembled without reactants, isolated from the helium tank (at a) and mercury bubbler (at b) and flamed with an air–gas torch. The vacuum line was then filled with helium gas, passed through two liquid nitrogen cold traps, and the reaction vessel (8) was removed at the Teflon Ultra-Torr Coupling[12] (7). In a dry box (~2 ppm H_2O and O_2 in a nitrogen atmosphere), reactants were ground together in appropriate proportions, mixed with glass beads, and put into the vessel. Once back on the vacuum manifold, the reaction vessel was again evacuated, and traps 1, 2, 3 were cooled to −140°C. U tube (4) was cooled with ice water, the system was filled with an overpressure of helium (a), and the mercury bubbler opened. The pressure was adjusted by the bubbler level and helium flow rate. An oil bath at 60°C was placed around the reaction chamber and its temperature was slowly raised to between 70 and 100°C. With vigorous shaking of the reaction vessel (at 6), reaction usually

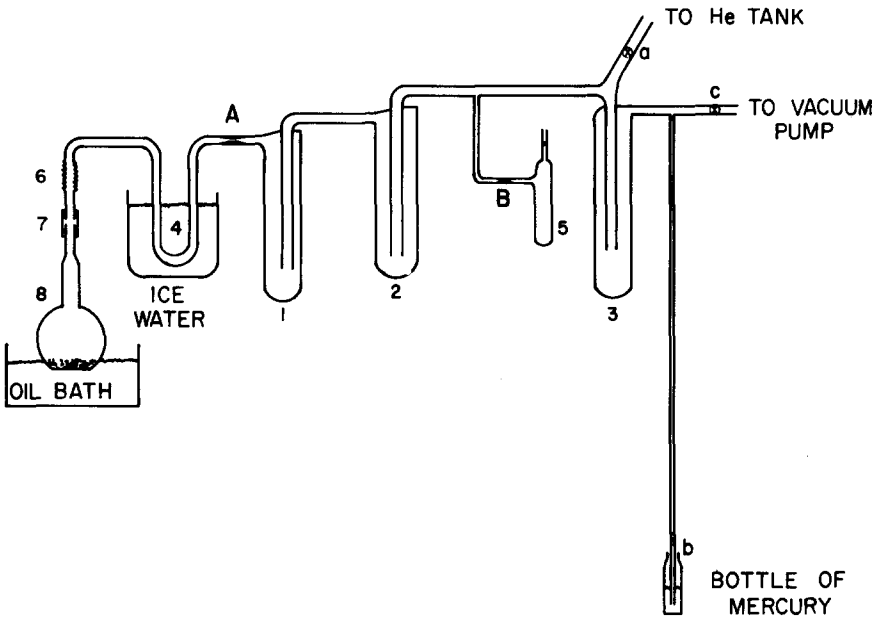

FIG. 3. Vacuum apparatus used for synthesis of borazine. (1), (2), (3) are cold traps; (4) U-tube to prevent reactants from being carried throughout system; (5) final break seal collection vessel; (6) flexible stainless steel-to-glass coupling used for shaking the reaction mixture; (7) teflon Ultra-Torr coupling-O-ring sealed connection for reaction vessel; (8) reaction vessel, typically a 500 ml boiling flask; (A), (B) are vacuum seal-off constrictions; (a), (b) are high vacuum stopcocks; (c) 1 in. stainless steel Teflon-packed ball valve to vacuum pumps and gauges.

commenced, as judged by rapid evolution of hydrogen gas through the mercury bubbler, in the range 70–90°C.

The oil bath temperature was gradually raised another 100°C, with the reaction eventually ceasing somewhat below 200°C. Reaction vessel and U tube containing entrained reactants were glass-blown off under vacuum (at A). The product was thoroughly degassed, transferred to collection vessel 5, and glass-blown off the system under vacuum. Over-all yield was generally about 30%; this low yield is probably due to severe caking of the reaction mixture.

The product of the above process, impure borazine, was stored in darkness at 77°K until used. When needed, the borazine was differentially vacuum distilled through a number of traps to remove both more and less volatile impurities and decomposition products. After a final series of distillations in a third manifold, purified borazine was transferred into breakseal tubes of appropriate size and again stored in darkness at 77°K. Thus obtained, borazine melted at −55°C (as observed visually) and evidenced an NMR spectrum characteristic of borazine. The vapor pressure of borazine is roughly as reported in the literature. When left standing at 300°K for about a week, our borazine "melted" (appeared to melt) at higher temperatures, eventually turning into cloudy white syrup and finally solidifying completely at 300°K. It should be noted, however, that in spite of this drastic physical change in borazine, its observed NMR spectrum remained invariant.

B. Spectroscopic Techniques and Apparatus

The absorption spectrum of gas phase borazine was taken both photographically and photoelectrically on a 2.0 m, $f/17$, McPherson vacuum ultraviolet, Czerny–Turner spectrograph. This instrument gives a first order dispersion of 4 Å/mm at the exit plane. Wave length calibration (±0.1 Å) was achieved by superimposing a mercury standard in first order (4000 Å–3000 Å) on a second order molecular hydrogen discharge. Due to poorly resolved and broad absorption lines, it was found that best estimates of line position (both absolute and relative) could be obtained photoelectrically by calibration of a wave length drive output marker.

Bolted on axis to the entrance slits of the spectrograph were, in order, a flange with a Suprasil quartz

TABLE I. Theoretical calculations of (π–π^*) transitions energies for borazine (in eV).

Calculation	$^1A_2'$	$^1A_1'$	$^1E'$
Roothaan (1948)[a]	6.5	7.2	7.7
Davies (1960)[b]	5.7	6.1	8.8
Chalvet (1965)[c]	6.51	5.74	7.14
Perkins (1966)[d]	6.58	7.26	7.51
Kuznesof (1968)[e]	8.48	9.65	9.86
Peyerimhoff (1970)[f]	7.88	9.02	9.59
Young (1971)[g]	6.52	7.84	7.3
Observed[h]	(7.0)	6.5	7.5

[a] Reference 7.

[b] D. W. Davies, Trans. Faraday Soc. **56**, 1713 (1960).

[c] Reference 8, Method I.

[d] P. G. Perkins and D. H. Wall, J. Chem. Soc. (1966) **A**, 235.

[e] P. M. Kuznesof and D. F. Shriver, J. Am. Chem. Soc. **90**, 1683 (1968).

[f] Reference 9.

[g] W. F. Young, F. Green, J. Passmore, and I. Unger, Can. J. Chem. **49**, 233 (1971).

[h] Position of intensity maxima for $^1A_1'$ and $^1E'$. Position of $^1A_2'$ is guessed, based on discussion in the text, to lie between $^1A_1'$ and $^1E'$.

TABLE II. Absorption spectrum of borazine in vacuum UV.

λ (vac) ±0.1 Å	ν (cm⁻¹) (vac)	Relative intensity	Identifying method[a]	Progression[b]	ΔE′ ν′−ν(0−0) cm⁻¹	Harmonic values	Vibronic assignment[c] [ν(0−0) = 50 628±cm⁻¹]
2011.4	49 717	vw	*p*	2*	−911		$0-\nu_8''$
2006.0	49 850	?	*p*		−778		$(0-\nu_{19}'')$
2003.6	49 910	vw	*p*	3*	−718		$0-\nu_9''$
1995.6	50 110	s	*b*	1*	−518		$0-\nu_{17}''$
1990.6	50 236	w	*p*	4*	−392		$0-\nu_{10}''$
1978	50 556	vw	*p*		−72		$(\nu_{17}'-\nu_{17}'')$
1969	50 787	vw	*p*	4	159		$\nu_{10}'-0$
1961.9	50 971	s	*b*	1	343		$(\nu_{13}'-0)$ / $(\nu_{17}'-0)$
1956.0	51 124	vw	*p*	3	496		$\nu_9'-0$
1944.6	51 424	m	*b*	2	796		$\nu_8'-0$
1936.3	51 645	vw	*p*	4	1017	51 655	$\nu_4'+\nu_{10}'-0$
1929.0	51 840	s	*b*	1	1212	51 839	$\nu_4'+\nu_{17}'-0$
1923.3	51 994	w	*f*	3	1366	51 992	$\nu_4'+\nu_9'-0$
1912.6	52 285	m	*b*	2	1657	52 292	$\nu_4'+\nu_8'-0$
1908.3	52 403	w	*p*	5	1775		$(\nu_4'+\nu_{15}')-0$ / $(\nu_4'+\nu_{16}')-0$
1904.5	52 507	vw	*p*	4	1879	52 491	$2\nu_4'+\nu_{10}'-0$
1897.3	52 706	s	*b*	1	2078	52 707	$2\nu_4'+\nu_{17}'-0$
1891.6	52 865	m	*f*	3	2237	52 865	$2\nu_4'+\nu_9'-0$
1890.0	52 910	m	*f*	3	2282	52 905	$\nu_3'+\nu_4'+\nu_9'-0$
1881.0	53 163	m	*b*	2	2535	53 160	$2\nu_4'+\nu_8'-0$
1877	53 277	vw	*p*	5	2649	53 271	$2\nu_4'+\nu_{16}'-0$
1866.3	53 582	s	*b*	1	2954	53 575	$3\nu_4'+\nu_{17}'-0$
1859.3	53 784	m	*f*	3	3156	53 778	$\nu_3'+2\nu_4'+\nu_9'-0$
1857.6	53 833	m	*b*	3	3205	53 828	$2\nu_3'+\nu_4'+\nu_9'-0$
1850.1	54 051	m	*b*	2	3423	54 028	$3\nu_4'+\nu_8'-0$
1845.2	54 195	vw	*p*	5	3567	54 189	$\nu_3'+2\nu_4'+\nu_{16}'-0$
1836.6	54 448	vw	*p*	1	3820	54 443	$4\nu_4'+\nu_{17}'-0$
1828	54 705	vw	*p*	3	4077	54 696	$2\nu_3'+2\nu_4'+\nu_9'-0$
1819.2	54 969	w	*p*	2	4341	54 946	$\nu_3'+3\nu_4'+\nu_8'-0$
1814	55 127	vw	*p*	5	4499	55 107	$2\nu_3'+2\nu_4'+\nu_{16}'-0$
1799	55 586	vw	*p*	3	4958	55 564	$2\nu_3'+3\nu_4'+\nu_9'-0$

[a] *p* = photomultiplier tube recording. *f* = film. *b* = both film and photomultiplier tube.

[b] See text.

[c] Vibration numbering system is given in Table IV. Assignments in parentheses are uncertain. The line at 50 971 cm⁻¹, the vibronic origin of Progression 1, can be associated with ν_{13}' or ν_{17}'. Other members of Progression 1, built on this origin, retain this ambiguity. Similarly, Progression 5 can be otherwise interpreted as based on ν_{15}' or ν_{16}' (see text).

window, a 15.0 cm aluminum gas cell, another flange with a Suprasil quartz window, and a hydrogen discharge light source. Initially LiF windows were used. It was found, however, that decomposition of borazine on the windows under these irradiation conditions, was so severe that quartz windows were superior to the more highly transparent LiF. The gas cell was evacuable to about 5×10^{-7} mm Hg by means of a portable vacuum system, attached through copper tubing. Borazine, freshly vacuum distilled, was attached to this manifold through a brass bellows valve and an Ultra-Torr Coupling. The break-seal tube containing the sample was kept under liquid nitrogen and covered with a cloth at all times prior to warm up for admission into the absorption cell. Borazine vapor pressure was controlled by a temperature bath placed around the break-seal tube.

The molecular hydrogen discharge light source provided an excellent flat continuum between 2300 Å and 1700 Å. This proved particularly helpful in locating weak absorption features. The multiplier phototube used was an EMR-541-DO5-14-M6 with a sapphire window and bialkali photocathode. The associated electronics and housing were designed for photon counting and will be described in detail in a forthcoming publication.[13] Kodak SWR film was used for photographic detection.

An unsuccessful attempt to observe emission from gas phase borazine was made. However, this result must not be viewed as definitive. Many improvements in experimental techniques are currently under investigation. Nonetheless, it is possible to conclude that emission from borazine is quite weak.

Data from absorption experiments are presented in

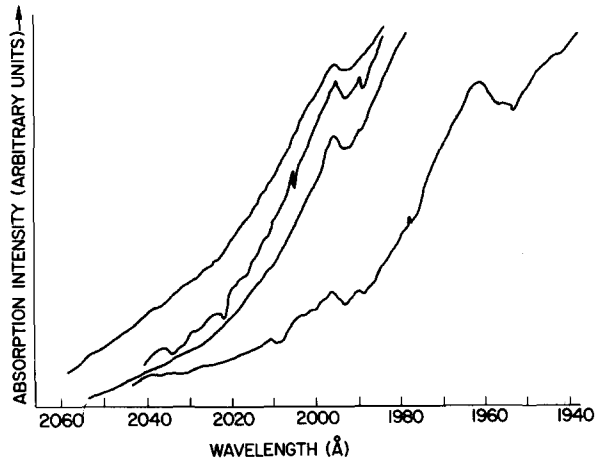

FIG. 4. Representative photomultiplier tube tracings of 2000 Å system absorption of borazine. Assigned features are presented in Table II.

Table II and Figs. 4–6 contain representative photomultiplier-strip chart recorder histograms. Photographic plates and their optical density recordings (Fig. 7 and 8) show the same data with sometimes more and sometimes slightly less clarity. The spectrograph slits were usually 20–50 μm giving a resolution of 0.1 Å or about 3 cm^{-1} in first order. All recorded data were obtained at this resolution.

IV. ANALYSIS OF THE ABSORPTION SPECTRUM

A. Vibronic Coupling Theory and the Assignment of State Symmetry

As discussed in Sec. II, the low lying $\pi\pi^*$ excited states are of $^{1,3}A_1'$, $^{1,3}A_2'$, $^{1,3}E'$ symmetry in the D_{3h} point group. Only the $^1E'$ state is dipole (x, y) allowed (see Fig. 2). Considering only singlet manifolds then, $^1A_1'$ and $^1A_2'$ states can "borrow" intensity through vibronic coupling to $^1E'$ (x, y) $\pi\pi^*$ state. A state of $^1A_2''$ (z) symmetry could also lend dipole character through vibronic coupling but since this state does not

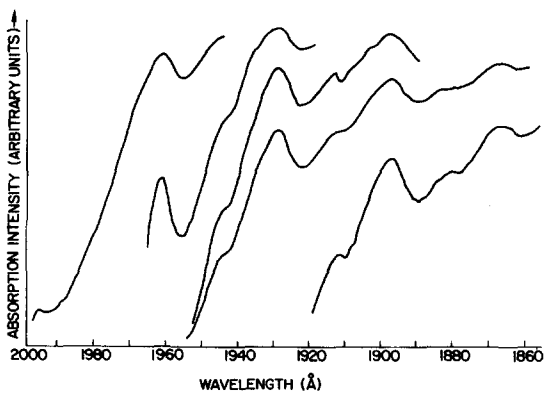

FIG. 5. Representative photomultiplier tube tracings of 2000 Å system absorption of borazine. Assigned features and progressions are given in Table II.

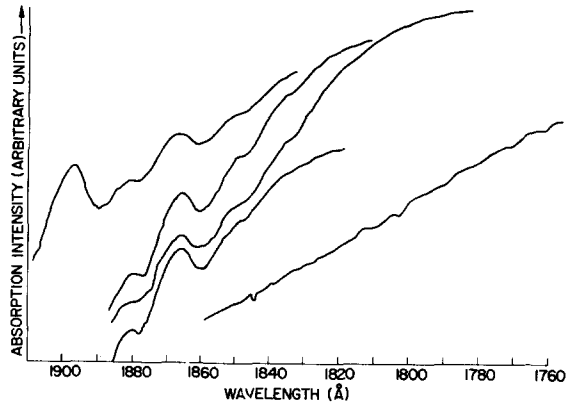

FIG. 6. Representative photomultiplier tube tracings of 2000 Å system absorption of borazine. Assigned features are presented in Table II.

arise from a "first excited state" of the π system, it is to be expected that this vibronic coupling route would be less effective in bringing in intensity than the $^1E'$ one. Table III summarizes these intensity enhancement mechanisms.

Thus, one very interesting conclusion is to be reached through this argument (Table III). It is possible to uniquely distinguish between the $^1A_1'$ and $^1A_2'$ states of borazine (corresponding to $^1B_{1u}$ and $^1B_{2u}$ states of benzene, respectively) by the appearance of a_2'' vibrational modes in absorption or emission spectra. If both a_2'' and e' vibrations are observed in absorption, as either hot bonds or excited state modes, the transition is of $^1A_1' \leftarrow {}^1A_1'$ character in D_{3h} symmetry.

B. Ground State Vibrational Assignments

In order to analyze absorption or emission spectra of borazine, ground state vibrational assignments must be made. A number of workers have published ground state vibrational data and interpretations.[14–17] Unfortunately, they disagree on some vibrational assignments and values. It was therefore necessary to look into techniques and methods to choose a "best set" of ground state frequencies. Since the present work deals only with gas phase borazine, gas phase frequencies

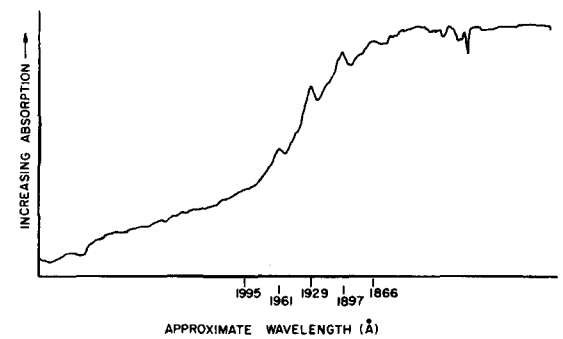

FIG. 7. Densitometer tracings of photographic film spectra of 2000 Å system absorption of borazine. See Table II for assignments.

are given preference. These various data are collected in Table IV; frequencies and normal mode assignments used in the present work are therein identified. Luckily, vibrations of central importance to our results appear to be uncontested. In order to get some feel for the correctness of these assignments, it is helpful to compare them to benzene vibrations, especially different (D_{3h} and D_{6h}) isotopes. While there cannot be a one-to-one correlation between C_6H_6–$B_3N_3H_6$, and C_6D_6–$B_3N_3D_6$ vibrations due to mode mixing in reduced symmetry, such a comparison is indeed informative. In Table V ground state vibrations for C_6H_6, C_6D_6, $B_3N_3H_6$, $B_3N_3D_6$ along with their appropriate ratios are listed. It is clear that little mode mixing is involved for a_1' and e'; substantial mixing occurs, however, for e_{1g} and e_{2u} D_{6h} vibrations in e'' D_{3h} symmetry. From this, it is concluded that no gross or obvious misassignments of borazine vibrational modes have been made.

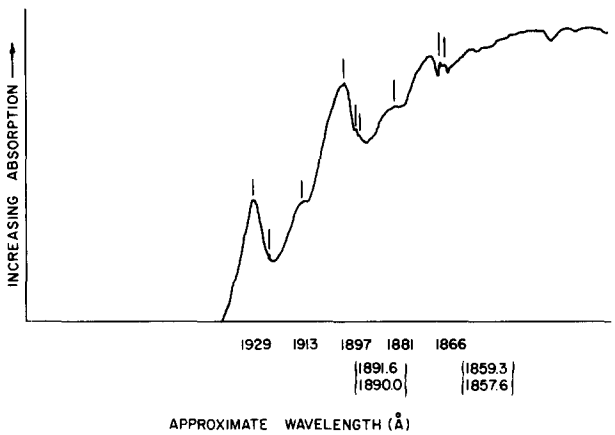

FIG. 8. Densitometer tracing of photographic film spectra of 2000 Å system absorption of borazine. See Table II for assignments.

C. First Order Vibronic Analysis of Absorption Spectrum

Data obtained from gas phase absorption of 15 cm of borazine at pressures from ~0.1 to ~5 mm Hg are presented in Table II. These data can be interpreted on the basis of five separate progressions in totally symmetric vibrations built on "false" or vibronic origins. The key to this decomposition is four observed hot bands (see Fig. 4). Progressions 1–5 are listed in Table II.

The 1995.6 Å absorption is identified as a hot band from its temperature dependence and in comparison to absorption spectra of other molecules.[3,18] Although this peak is of rather low intensity, it is stronger than other potential hot bands around it; logically then it is assumed to be a member of the strongest series in borazine's spectrum, Progression 1 (Fig. 4). The six members of Progression 1 are 1995.6 Å, 1961.9 Å, 1929.0 Å, 1897.3 Å, 1866.3 Å, and 1836.6 Å. Under these assumptions the 861 cm^{-1} initial spacing in this series must be composed of the sum of a ground and excited state vibration of either class e' or a_2'' (see Table III). Considering that this state is nondegenerate and transitions from the ground state to it are dipole forbidden, the most "logical" possibility for this separation is ν_{17}'' (518 cm^{-1}) in the ground state plus ν_{17}' (343 cm^{-1}) in the excited state. In anticipation of future discussion, however, choice of ν_{17}' as excited vibronic origin of Progression 1 may well be *incorrect* for the $^1A_1'$ state (corresponding to $^1B_{1u}$ state of benzene). Arguments in favor of a different assignment of the 1961.9 Å feature are complex, take some space to develop, and will be detailed in the following section.

The remaining features in this series are totally

TABLE III. Enabling vibrations for various vibronic coupling routes in borazine.

Borazine transition	0–0 character	Vibronic coupling route $^1A_2''(z)$	Vibronic coupling route $^1E'(x, y)$
$^1A_1' \rightleftarrows {}^1A_1'$	Dipole forbidden	a_2''	e'
$^1A_1' \rightleftarrows {}^1A_2'$	Dipole forbidden	none	e'
$^1A_1' \rightleftarrows {}^1E'$	(x, y) dipole allowed	...	...

TABLE IV. Borazine ground state normal modes (in cm^{-1}). (Numbers in boldface are the ones used in this work.)

Label (ν_i)	Symmetry species	Kaldor[a]	Niedenzu[b]	Silberman[c]
1	a_1'	**3488**	3452	
2	a_1'	**2545**	2535	
3	a_1'	**942**	940	
4	a_1'	**857**	852	
5	a_2'	...		
6	a_2'	**1195**		
7	a_2'	**782**		
8	a_2''	913	**917.5**	1088
9	a_2''	718	**719**	649
10	a_2''	403	**394**	415
11	e'	3482	**3486**	3490
12	e'	2513	**2520**	2530
13	e'	1458	**1465**	1605
14	e'	1394	**1406**	1465
15	e'	1102	**1096**	918
16	e'	1068	**990**[d]	718
			1068(?)	
17	e'	518	**518**	519
18	e''	**987**	968	
19	e''	**787**	798	
			1070(?)	
20	e''	**280**	288	

[a] Reference 14.
[b] Reference 15, 17.
[c] Reference 16.
[d] The difficulty with ν_{16} assignment is not resolved. See Refs. 14–17.

TABLE V. Ground state vibrations of benzene, borazine, and their deuterated species.[a]

D_{6h} label (ν_i)	C_6H_6[b]	C_6D_6[b]	D_6/H_6	D_{3h} label (ν_i)	$B_3N_3H_6$[c]	$B_3N_3D_6$	D_6/H_6
	a_{1g} and b_{1u}				a_1'		
ν_1	995.4	945.6	0.950	ν_4	857	824	0.966
ν_{12}	1010	970	0.960	ν_3	942	901	0.958
ν_{13}	3057	2285	0.747	ν_2	2545	1895	0.747
ν_2	3073	2303	0.749	ν_1	3488	2567	0.743
	a_{2g} and b_{2u}				a_2'		
ν_{15}	1146	824	0.719	ν_7	782		
ν_{14}	1309	1282	0.979	ν_6	1195		
ν_3	1350	1059	0.784	ν_5	...		
	b_{2g} and a_{2u}				a_2''		
ν_{11}	674	496.2	0.735	ν_{10}	394	323	0.819
ν_4	707	599	0.847	ν_9	719	540	0.751
ν_5	990	829	0.837	ν_8	917.5	782.5	0.853
	e_{1g} and e_{2u}				e''		
ν_{16}	398.6	347.4	0.871	ν_{20}	280	255	0.885
ν_{10}	846	660	0.780	ν_{19}	787	550	0.690
ν_{17}	967	787	0.813	ν_{18}	987	723	0.746
					1068(?)	812	0.760
	e_{2g} and e_{1u}				e'		
ν_6	608	580.2	0.954	ν_{17}	518	499	0.963
ν_{18}	1037	814	0.894	ν_{16}	990	766.5	0.774
					1068(?)	860(?)	0.760
ν_9	1178	869	0.737	ν_{15}	1096	797	0.727
ν_{19}	1482	1333	0.899	ν_{14}	1406	1245	0.921
ν_8	1596	1558	0.976	ν_{13}	1465	1418	0.967
ν_7	3056	2274	0.744	ν_{12}	2520	1895	0.751
ν_{20}	3064	2288	0.747	ν_{11}	3486	2582	0.740

[a] The vibrations of each species are grouped in order of increasing frequency. There may or may not be a one-to-one correspondence between the benzene and borazine vibrations on any given line (e.g., there apparently is for the e' vibrations but is not for the a_2'' modes).

[b] Reference 3.

[c] See Table IV.

[d] The deuterated data is from Refs. 15 and 17.

symmetric ν_4' (868 cm^{-1}) additions to the false vibronic origin ν_{17}' (ν_{13}') at 1961.9 Å (50 971 cm^{-1}). At this point upper state symmetry can be assigned as either $^1A_1'$ or $^1A_2'$, but its true origin (0–0 position) is known to be 50 628±5 cm^{-1}.

Knowing the origin, it is possible to assign Progression 2 (2011.4, 1944.6, 1912.6, 1881.0, 1850.1, 1819.2 Å), if an e' or a_2'' vibration of 790 cm^{-1} can be assigned for the excited state. ν_8' (790 cm^{-1}) was chosen as the best possibility; it is immediately obvious that the feature at 2011.4 A is a ν_8'' (913 cm^{-1}) hot band. Progression 2 then consists of a ν_8'' hot band and a ν_8' excited state vibronic origin with totally symmetric ν_4' (868 cm^{-1}) and ν_3' (918 cm^{-1}) built on this false origin. *Since* ν_8 *has symmetry* a_2'', *the excited state is identified as* $^1A_1'$ *in* D_{3h} *symmetry.*

Progression 3 can be identified in a similar fashion as arising from a $\nu_9'(a_2'')$ false origin and a ν_9'' hot band at 2003.6 Å. The remainder of the lines in Progression 3 are due to ν_3' (918 cm^{-1}) and ν_4' (868 cm^{-1}) totally symmetric additions to the vibronic state at 1956.0 Å. Figure 8 best displays the dominant features of Progression 3.

Progression 4 is a collection of much weaker peaks than those described above. The hot band at 1990 A once again fits perfectly with 50 628 cm^{-1} predicted $^1A_1'$ origin when assigned to $\nu_{10}''(a_2'')$ with an energy of 394 cm^{-1}. ν_{10}', excited state vibronic origin at 1969 Å

has a frequency of 157 cm^{-1}. With this assignment, all a_2'' out-of-plane ground state modes, ν_8'', ν_9'', ν_{10}'', have been identified.

Finally, Progression 5 can be developed if one postulates existence of a hidden band at 1940.5 Å. This unresolved band could very well be either e' mode ν_{16}' or ν_{15}'. This latter choice is based on arguments to be presented in the next section. In either case totally symmetric additions of ν_3' and ν_4' fit in nicely with these assumptions.

It should be noted that all observed progressions can be assigned logically on the basis of a single excited electronic state. A summary of excited state vibrational assignments can be found in Table VI.

D. Borazine, Benzene, the Jahn–Teller Effect, and the Excited $^1A_1'$ Vibrational Assignments

In Sec. IV.C has been presented a conventional vibronic analysis and concomitant excited state vibrational assignments for borazine's first excited singlet state $^1A_1'$. While these two features of the last section are basically unrelated, it is important to understand their mutual consequences, particularly in light of the closely related and often compared spectrum of benzene.[3,4,7,19,20]

It was pointed out that $^1A_1'$ of borazine (D_{3h}) correlates to $^1B_{1u}$ of benzene (D_{6h}) and $^1A_2'$ of borazine correlates to $^1B_{2u}$ of benzene. Therefore, the bands under consideration correspond to the 2080 Å system ($^1B_{1u}\leftarrow{}^1A_{1g}$)[21,22] or the 3370 Å system ($^3B_{1u}\rightleftarrows{}^1A_{1g}$)[4,19,20] of benzene. Unfortunately this leaves the problem of location of the $^1A_2'$ state. It must be concluded that this transition $^1A_2'\leftarrow{}^1A_1'$ lies either around 2600 Å (i.e., between 3000 Å and 2100 Å) and is too weak to be observed, or it is hidden under the $^1E'\leftarrow{}^1A_1'$ and $^1A_1'\leftarrow{}^1A_1'$ transitions.

If it is believed that comparisons between benzene and borazine are nevertheless to be strongly emphasized, then problems arise with excited state vibrational assignments for the D_{3h} $^1A_1'$. In benzene, the existence of the Jahn–Teller vibronic coupling interaction $^{1,3}B_{1u}$–$\nu_8(e_{2g})$–$^{1,3}E_{1u}$ has been carefully established and is well known.[19,20,21,23] The analogous interaction in borazine would be $^{1,3}A_1'$–$\nu(e')$–$^{1,3}E'$. Its occurrence would primarily affect one vibronic transition, the excited $^1A_1'$ false origin at 1961.9 Å (50 971 cm^{-1}). In the presence of a Jahn–Teller vibronic interaction, it is not clear with which $^1A_1'$ excited state vibration, $\nu_{17}'(e')$, $\nu_{13}'(e')$, or $\nu_{15}'(e')$, this feature should be identified. These modes correlate rather well to the three e_{2g} benzene modes, ν_6 (606 cm^{-1}-ground state), ν_8 (1595 cm^{-1}-ground state), and ν_9 (1178 cm^{-1}-ground state), respectively. (See Tables IV–VI for complete data on these modes.) Moffitt and Liehr[23] have given convincing demonstrations that vibronic coupling (an "odd" or "*ortho*" perturbation[23a]) to an E_{1u} state should affect the B_{1u} state of benzene to a much greater extent than the B_{2u}

TABLE VI. Borazine excited state vibrational assignments and comparison to benzene.[a]

Borazine				Benzene				
Vibration number (symmetry)	Ground $\nu''(^1A_1')^0$ (cm^{-1})	Excited $\nu'(^1A_1')$ (cm^{-1})	$\left[\frac{\nu''(^1A_1')^0}{\nu'(^1A_1')}\right]$	Vibration number (symmetry)	$\nu''(^1A_{1g})$ (cm^{-1})	$\nu'(^1B_{2u})$ (cm^{-1})	$\left[\frac{\nu''(^1A_{1g})}{\nu'(^1B_{2u})}\right]$	$\nu'(^3B_{1u})$ (cm^{-1})	$\left[\frac{\nu''(^1A_{1g})}{\nu'(^3B_{1u})}\right]$
$\nu_3(a_1')$	942	918	1.026	$\nu_{12}(b_{1u})$	1010	...	...	...	...
$\nu_4(a_1')$	857	868	0.987	$\nu_1(a_{1g})$	995	923	1.078	925	1.076
$\nu_8(a_2'')$	917	790	1.161	$\nu_{11}(a_{2u})$	674	514	1.311	...	...
$\nu_9(a_2'')$	719	495	1.453	$\nu_4(b_{2g})$	707	365	1.937	382	1.851
$\nu_{10}(a_2'')$	394	157	2.516	$\nu_5(b_{2g})$	990	775	1.277	612	1.618
$\nu_{15}(e')$[b]	1096	905	1.211	$\nu_9(e_{2g})$	1178	950	1.239	1188	0.992
$\nu_{16}(e')$	990		1.094	$\nu_{18}(e_{1u})$	1037	...	...	...	...
$\nu_{13}(e')$[b]	1465	343	4.271	$\nu_8(e_{2g})$	1595	...	...	239 252	6.497
$\nu_{17}(e')$	518	1.510		$\nu_6(e_{2g})$	608	522	1.161	628	0.965
$\nu_{11}(e')$[b]	518	446	1.161						

[a] References 3, 4, 19, 20.
[b] Assignment uncertain. See text for discussion.

state, a fact which has been conclusively demonstrated by at least three different techniques.[19,20,23e–h] Since the first excited singlet state of borazine is $^1A_1'$ in D_{3h} symmetry ($^1B_{1u}$ in D_{6h}), such large vibronic coupling effects may, in view of this parallel, also be present in borazine absorption spectra of the 2000 A system under discussion. Three main features can be extracted from these previous benzene studies: (a) $\nu_8''(e_{2g})$ (1595 cm^{-1}) is the prominent feature in the 3370 Å system of benzene; (b) ν_8' in $^3B_{1u}$ is depressed in energy to about 245 cm^{-1} and splits due to the strong vibronic Jahn–Teller coupling $^3B_{1u}-\nu_8'(e_{2g})-{}^3E_{1u}$; and (c) out-of-plane vibrations (of b_{2g} symmetry in D_{6h} and a_2'' in D_{3h}) ν_4 and ν_5 serve as secondary false vibronic origins.

Moffitt's original work on "odd" and "even" perturbations dealt with catacondensed hydrocarbons.[23a] It is, however, straightforward to conclude that this theory, considering its approximate form and basic structure, is applicable to π-electronic states of the analogous *B–N* series and therefore borazine (see discussion of Sec. II). Working within this parallel, it is possible that the excited $^1A_1'$ vibronic origin of Progression 1 is $\nu_{13}'(e')$ instead of the "more conventional" assignment of this origin to $\nu_{17}'(e')$. This ambiguity is reflected in Table VI which summarizes the excited state vibrational modes identified in the present research (see for comparison Ref. 19 and Table VI). Within the confines of the present gas phase study and theoretical treatments of borazine which are far less intensive and accurate than those for benzene, it is not sensible to distinguish between the possible vibronic assignments for the excited state. Solution to this problem may come from our study of single crystals of borazine at 4.2°K.

V. GENERAL DISCUSSION AND CONCLUSIONS

(1) *The 2000 Å system, the first observed transition of borazine in the vapor phase, is* $^1A_1'\leftarrow{}^1A_1'$. Since roughly 25 μm to 3 mm crystals of borazine evidence no absorption to 2100 A[24] and high pressure (1 atmosphere) borazine experiments show no new absorptions appearing, we conclude that $^1A_2'\leftarrow{}^1A_1'$ is buried under the $^1A_1'\leftarrow{}^1A_1'$ and $^1E'\leftarrow{}^1A_1'$ transitions. Vibronic coupling theory[23] indicates the $^1A_1'\leftarrow{}^1A_1'$ should be more intense than the $^1A_2'\leftarrow{}^1A_1'$.

(2) The origin of this system lies at 50 628±5 cm^{-1} in the gas phase. The error is estimated on the inability to locate accurately positions of weak, broad lines.

(3) Excited state vibrational frequencies known with reasonable certainty are the first five listed in Table VI: $\nu_3'(a_1')=918$ cm^{-1}, $\nu_4'(a_1')=868$ cm^{-1}, $\nu_8'(a_2'')=790$ cm^{-1}, $\nu_9'(a_2'')=495$ cm^{-1}, and $\nu_{10}'(a_2'')=157$ cm^{-1}.

(4) A sizable fraction of the total $^1A_1'\leftarrow{}^1A_1'$ intensity is associated with out-of-plane a_2'' modes ν_8, ν_9, ν_{10}.

(5) Anharmonicities associated with totally symmetric additions to false (vibronic) origins ($n\nu_3'$ and $n\nu_4'$ of Progressions 1–5) are small and mostly obscured by data scatter and inaccuracies in positions of intrinsically broad and unresolved lines.

(6) Two vibronic origins in the excited state cannot be identified with certainty due to a theoretically possible vibronic Jahn–Teller coupling with the $^1E'$ excited state less than 10 000 cm^{-1} to higher energy. Both these vibrations, given in Table VI, are of appropriate e' symmetry. In the absence of a vibronic Jahn–Teller interaction between $^1A_1'$ and $^1E'$, one could, based on conventional vibronic analysis arguments, assign these vibrations as $\nu_{17}'(e')=343$ cm^{-1} and $\nu_{16}'(e')=905$ cm^{-1}. Clearly however, if one assumes large Jahn–Teller effects in the excited state, only totally symmetric modes ν_3' and ν_4' are positively identified. In this regard, much weight is placed on the benzene parallel, both to substantiate the presence and limit the size of vibronic perturbations.

(7) Absorption spectra of $^1B_{1u}\leftarrow{}^1A_{1g}$ transition of benzene (2080 Å system)[21] and $^1A_1'\leftarrow{}^1A_1'$ (2000 Å system) of borazine are superficially quite similar. Indeed, this observation alone initially led Platt and co-workers[22a] to conclude the borazine upper state was $^1A_1'$. From vibronic coupling theory as put forward by Moffitt and Liehr,[23] two predictions follow directly from this assignment. The $^1A_1'$ transition should be more than a factor of 10 times as intense as $^1A_2'\leftarrow{}^1A_1'$ and a Jahn-Teller distortion, vibronically "borrowed" from $^1E'$, should appear in *at least one* normal coordinate, $\nu_{13}(e')$. This mode corresponds to ν_8 (e_{2g}, C–C stretch, 1595 cm^{-1} in $^1A_{1g}$) in benzene; ground state frequency for ν_{13}'' is 1465 cm^{-1}.

The benzene 3370 Å system ($^3B_{1u}\leftarrow{}^1A_{1g}$) is taken as the model for the $^1A_1'\leftarrow{}^1A_1'$ borazine transition because of inherently low information content in the comparable $^1B_{1u}\leftarrow{}^1A_{1g}$ transition. This spin forbidden transition is characterized by totally symmetric progressions built on false vibronic origins of $b_{2g}(\nu_4, \nu_5)$ and e_{2g} (ν_6, ν_8, ν_9) symmetry. The Jahn–Teller nature of $^3B_{1u}$ is seen only in the excited ν_8' frequency, and its associated effect on the zero point motion. See Table VI for comparison of these vibrations.

While comparisons are in many instances dangerous and always have their limitations, some of the more interesting features of the borazine excited $^1A_1'$ state and the $^1A_1'\leftarrow{}^1A_1'$ transition are brought out by comparison to benzene spectra. We are driven to this parallel not by choice but by necessity; simply stated, neither borazine data nor theoretical studies are of sufficient quality to stand on their own. Hopefully, only the experimental situation is intrinsic. To place this comparison in its proper light, it should be reiterated that the order of states for benzene consistently predicted theoretically and found experimentally, is $^1B_{1u}$, $^1B_{2u}$, $^1E_{1u}$. The order in borazine, arising in similar manner from the identical orbital set is most probably $^1A_1'(^1B_{1u})$, $^1A_2'(^1B_{2u})$, $^1E'$ ($^1E_{1u}$), with corresponding

D_{6h} benzene states given in parentheses. This difficulty or lack of parallelism notwithstanding, substantial positive gain in terms of understanding and predictability comes from viewing benzene and borazine together. In particular, this comparison underscores the caution with which an excited state vibronic analysis of borazine must be approached.

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Self-Diffusion Coefficients and Rotational Correlation Times in Polar Liquids. V. Cyclohexane, Cyclohexanone, and Cyclohexanol*

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Self-diffusion coefficients and proton and deuteron relaxation times have been measured in cyclohexane (C_6H_{12}), cyclohexanone ($C_6H_{10}O$), and cyclohexanol ($C_6H_{12}O$). The results are interpreted with the quasi-lattice random flight (QLRF) model and a dynamical rotational coherence (DRC) theory, a general formulation of which is given in the present paper. The experiments were carried out to ascertain the effect of adding (1) a large dipole moment and (2) a strong hydrogen bond to the cyclohexane molecule. Molecular reorientation or self-diffusion are not greatly affected by the addition of dipole moment but become more than an order of magnitude slower in cyclohexanol. The results of DRC and QLRF models are compared with experiment for a wide variety of liquids.

I. INTRODUCTION

The present research is concerned with the rate and mechanism of molecular rotation in liquids. The lack of agreement of the Stokes–Einstein–Debye continuum model of rotational diffusion with experimental rotational correlation times (τ_2) led O'Reilly and Schacher[1] to propose that large amplitude molecular rotation occurs upon a hard collision in the liquid at an interstitial site. It was assumed that molecular rotation is relatively slow in the time between collisions. This model was later refined[2] with the aid of the theory of finite step rotational Brownian motion and it was demonstrated that it yielded reasonable results for a wide variety of liquids. A clear exception to this model occurred for liquid hydrogen chloride which appeared to be undergoing continuous inertial rotation in a manner somewhat similar to that proposed by Steele.[3] However an important difference between the interpretations was that Steele assumed that the correlation function of the inertial rotation would have a Gaussian decay while in Ref. 2 it was