

Absorption Spectra and Ionization Potentials of Benzene and Benzened 6

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TABLE I. Observed and calculated frequencies for the tritiated water molecules.

Molecule	Assignment	Observed frequency	Anharmonicity correction	ω_{observed}	$\omega_{\text{calculated}}$
T ₂ O	ν_2	995.5	C	21.7	1017.2
	ν_8	2370 \pm 5	C	68.3	2438 \pm 5
		2364	Q		2436.1
	$\nu_2 + \nu_8$	3420 \pm 5	R		
		3358	Q		
		3295 \pm 5	P		
	$\nu_1 + \nu_8$	4602 \pm 5	R		
		4537	Q		
		4481 \pm 5	P		
THO	ν_2	1324	C	34.8	1358.8
	ν_8	3720 \pm 10	C	174.7	3895 \pm 10
		3711	Q		3882.6
TDO	ν_8	2792 \pm 5	R		
		2735 \pm 5	C	93.7	2829 \pm 5
		2730	Q		2830.7
		2670 \pm 5	P		

values of ω_{ij} so obtained are compared with the fundamental frequencies calculated by Libby from the potential function and force constants of H₂O. The agreement is considered satisfactory, although the discrepancy for ν_2 of THO, 16 cm⁻¹, is definitely greater than the estimated error in locating the band center.

† Based on work performed for the U. S. Atomic Energy Commission by Union Carbide Nuclear Company, a Division of Union Carbide and Carbon Corporation, at the Oak Ridge National Laboratory.

¹ W. F. Libby, J. Chem. Phys. 11, 101 (1943).

Absorption Spectra and Ionization Potentials of Benzene and Benzene-*d*₆†

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THE absorption spectra of benzene and benzene-*d*₆ in the vacuum ultraviolet have been photographed recently in this laboratory using the first order of a 21-ft concave grating spectrograph (dispersion 1.3 Å/mm). The use of the xenon¹ and krypton² continua as absorption backgrounds greatly facilitated the identification of many new weak bands which were not apparent in the previous work of Price and Wood,³ who employed the Lyman continuum as the source.

Four Rydberg series, each with 8 to 10 members, were identified using the following criteria for each member: (1) strong intensity for the "vibrationless" transition; (2) isotope shift on deuterium substitution about 35 cm⁻¹ toward higher frequencies; and (3) similar vibrational structure. All four series were found to converge to the same ionization potential: 9.247 \pm 0.002 eV (C₆H₆) and 9.251 \pm 0.002 eV (C₆D₆). The results are in agreement with recent electron impact measurements,⁴ and in especially good agreement with recent photoionization measurements (9.245 \pm 0.01 eV).⁵

Vibrational progressions of the $\nu_2(a_{1g})$, $\nu_{18}(e_{2g})$, and $\nu_{20}(e_{2u})$ vibrations were found to be associated with each Rydberg transition except those in the confusing region close to the ionization limit. The ν_2 totally symmetric vibration was previously identified,³ and has a value of 974 cm⁻¹ for benzene and 922 cm⁻¹ for benzene-*d*₆ in a typical Rydberg state as compared to 992 cm⁻¹ and 945 cm⁻¹, respectively, in the ground state.⁶ Other vibrational progressions of about 696 cm⁻¹ (benzene) and 676 cm⁻¹ (benzene-*d*₆) in spacing, reported by Price and Wood,³ have been confirmed, but are reinterpreted as two quanta of the nontotally symmetric

ν_{18} vibration (606 cm⁻¹ and 577 cm⁻¹ in the ground state⁶), from their magnitudes, isotope effect, and observation of weak "hot" bands of the type $\nu_{18}'=1$ to $\nu_{18}'=3$. Other spacings to longer wavelengths of each main band are interpreted as 1-1, 2-2, . . . $v-v$ type "hot" bands of the nontotally symmetric ν_{20} progression from their intensity and isotope effect. This vibration has typical values of 314 cm⁻¹ (benzene) and 262 cm⁻¹ (benzene-*d*₆) as compared to 404 and 337 cm⁻¹, respectively, in the ground state.⁶ In addition, combination bands of the type $2\nu_{18}+\nu_{20}$ and $\nu_2+\nu_{20}$ are readily identified. In all, about 120 bands in each molecule were observed, and nearly all may be readily classified.

In all the Rydberg transitions the intensity of the ν_{18} (nontotally symmetric) progression is greater than or comparable with that of the ν_2 (totally symmetric) progression, and in some cases four series members can be identified. This may be interpreted in terms of the Jahn-Teller theorem⁷ if a nuclear displacement of e_{2g} symmetry is assumed in all of the excited Rydberg states.⁸ Since the ν_{18} vibration possesses symmetry e_{2g} , the intensity of such progressions would be expected to be enhanced, thus preserving the symmetry of the excited state. No Jahn-Teller splitting in the energy levels, corresponding to removal of degeneracy in the excited states, is observed. The foregoing interpretation represents the first experimental verification of the Jahn-Teller theorem and is significant because only an unusual intensity distribution is found. Complete details of the spectra, including vibrational constants and isotope effects in all observed states will be found in a paper to appear in an early issue of the Canadian Journal of Physics.

I wish to acknowledge the help of Professor R. S. Mulliken, Professor J. R. Platt, Professor C. C. J. Roothaan, and Professor L. E. Orgel in many discussions. I am indebted to Dr. L. C. Leitch of the National Research Council (of Canada) for the loan of a sample of benzene-*d*₆.

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⁸ In a private communication, Dr. L. E. Orgel of Cambridge University, England, disclosed that he had independently arrived at this same interpretation from studying our spectra.

Irradiation of Chloral Hydrate Solutions

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AQUEOUS solutions of chloral hydrate, CCl₃H(OH)₂, have been used to determine x-ray dosages on the basis of conductivity measurements using platinum electrodes.¹

In an effort to measure low dosages (below 1000 r) on these solutions, a Q-meter type experimental instrument, using an oscillating current up to 30 mc, developed by J. W. Kanwisher,² was employed for the conductivity measurements. Ordinary test tubes (13 mm diameter) were used to contain the solutions. The results confirmed the experiments of Andrews and Shore¹ that the more concentrated the solution of the chloral hydrate the greater the sensitivity to radiation.

It had been reported that glucose reacts in an "anomalous" way³ and its effects on biological process are different from other sugars.⁴ Conductivity measurements were made on solutions of glucose and chloral hydrate. Results are given in Table I.

In a dilute solution of chloral hydrate (0.5 M), a small amount of glucose (0.01 M) increased (almost doubled) the sensitivity of the solution to x-radiation, while in more concentrated solution of

TABLE I.

Solution	Units				
	Arbitrary on		Kanwisher device		
Roentgens (x-ray 200 kv, 10 ma, 0.01 in. Cu filter at 400 r increments)	0	400	800	1200	1600
Chloral hydrate 0.5 M	2.4	2.6	2.7	3.1	3.1
Chloral hydrate 0.5 M Glucose 0.01 M	4.3	5.4	6.3	7.0	8.0
Chloral hydrate 2.5 M	7.2	9.3	11.3	12.5	
Chloral hydrate 2.5 M Glucose 0.01 M	7.4	8.9	10.4	11.8	12.4
Chloral hydrate 2.5 M Glucose 0.1 M	7.8	7.8	7.8	8.1	8.1

chloral hydrate, 2.5 M, the same amount of glucose has little or no effect. Large amounts of glucose in solution had an inhibiting effect. The results were reproducible.

The reaction appears complex.¹ However, some explanation may be gleaned from the work of Dewhurst,⁵ who has shown that small quantities of aliphatic alcohols have a pronounced effect on the initial oxidation yield of ferrous sulfate. His explanation on the formation of a free radical and peroxide may hold for the effect of glucose on chloral hydrate.

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Rotational Magnetic Moment and Diamagnetic Susceptibility of Methane*

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IT has been shown by Wick,¹ Ramsey,² and Eshbach and Strandberg³ that the "high-frequency" term contributing to the diamagnetic susceptibility, χ , of a $^1\Sigma$ molecule may be obtained from a determination of its rotational magnetic moment. This moment is of the order of a nuclear magneton and may be measured by molecular-beam experiments² or, less accurately, from the Zeeman effect in the microwave spectrum.^{3,4} The "high-frequency" term involves the off-diagonal matrix elements for the total electronic orbital angular momentum about the magnetic field direction,⁵ and if it is written in terms of the rotational gyro-magnetic tensor elements, χ becomes

$$\chi_{\text{mole}} = \frac{Ne^2}{6mc^2} \left[- \sum_i \langle r_i^2 \rangle_{\text{av}} - \frac{1}{2M_p} \sum_{g=a,b,c} g_{gg}'' I_g \right], \quad (1)$$

where M_p is the mass of the proton, and I_g is the moment of inertia of the molecule about the principal axis g . Also g_{gg}'' is a diagonal member of the electronic part of the tensor and may be obtained from the measured quantity, g_{gg} , by subtracting off the nuclear contribution g_{gg}' (see reference 3 for this notation).

This paramagnetic contribution to χ is extremely difficult to calculate since it involves knowledge of the excited electronic states, and, except for H_2 ,⁶ it has generally been neglected. Such a procedure was followed by Buckingham, Massey, and Tibbs⁷ and Coulson⁸ in their calculations on CH_4 , and justified at that time by the near spherical symmetry of the molecule. Buckingham *et al.* used an approximate self-consistent field procedure and calculated the first term in Eq. (1) to be -33.2×10^{-6} emu. Coulson obtained a value of -26.6×10^{-6} from molecular orbital LCAO theory and -27.7×10^{-6} emu from the "electron-pairing"

approximation of valence bond theory. The experimental value of χ mole is -12.2×10^{-6} emu.⁹

Although the rotational magnetic moment of methane has not been measured, the value of g_{zz} (i.e., along the symmetry axis) of $\text{CH}_3-\text{C}\equiv\text{C}-\text{D}$ has been determined to be ± 0.31 from microwave Zeeman measurements.¹⁰ The π and σ electrons along the symmetry axis are in the cylindrical potential field about this axis and therefore do not contribute to g_{zz} . If it may be assumed that the methyl group electrons are unaffected when excitation takes place to the relatively low-lying excited states of the π electrons, then g_{zz} may be attributed to the motion of the CH_3 group alone. Hyperconjugation will have little effect upon the C-H bond characteristics¹¹ so that one may then take the value of g (since $g_{zz} = g_{yy} = g_{xx}$) for CH_4 to be that given in the foregoing. Then it also follows that the sign of the g -value must be positive simply because we are dealing with bonded rotating hydrogen nuclei.³

The nuclear contribution, $g' = +1.00$, may be subtracted out, and the second term in Eq. (1) is calculated to be $+9.3 \times 10^{-6}$ emu for CH_4 . The "experimental" value of the r^2 term now becomes -21.5×10^{-6} emu. Thus, the high-frequency term is about 40% of the diamagnetic one, and the assumption of complete "slippage" of the valence electrons was quite erroneous. Therefore, one concludes that the calculations of Buckingham *et al.* and Coulson are considerably more accurate than previously supposed, although they still yield too diffuse an electronic distribution. The important thing is that the simple molecular orbital and valence bond wave functions do give good values of $\langle r^2 \rangle_{\text{av}}$. It may be that a good fit of both the energy¹² and magnetic susceptibility data will lie within a reasonable range of variation of the parameters in Coulson's calculations.

I should like to thank Professor W. Moffitt for an informative discussion of this subject.

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Calculation of Potential Barriers for Ethane-Like Symmetric Tops

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THE final explanation of the magnitude of barriers hindering internal rotation in the molecules of Table I and others must be given in terms of electronic energy as a function of the torsional

TABLE I. Potential barriers in cm^{-1} for ethane and ethane-like molecules.

	Experimental ^a	Calculated in this paper
CH_3CH_3	960	913
CH_3CCl_3	1040 ^b	1142
CH_3CF_3	1200	1202
CH_3SiH_3	558	571
CH_3SiF_3	410	694

^a See reference 2.

^b Pitzer and Hollenberg, *J. Am. Chem. Soc.* **75**, 2219 (1953).