JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY
(Registered in U. S. Patent Office) ((C) Copyright, 1959, by the American Chemical Society)
VOLUME 81 JULY 17, 1959 NUMBER 13

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Chemically Induced Vibrational Excitation: A Study of Hydroxyl Radicals Formed in the H + O_3 Atomic Flame[1,2]

BY DAVID GARVIN

RECEIVED DECEMBER 8, 1958

The vibrational–rotational spectrum of the hydroxyl radical in its electronic ground state has been determined in the visible and near infrared region. Line systems in twenty-six vibrational bands have been identified. Intensities of lines in twenty one bands are reported. No evidence of a Boltzmann distribution of rotational energies among these chemically produced radicals was found. The vibrational band intensities show an inter-relationship that is not consistent with predictions based on the Morse Oscillator transition moment expressions. Further developments are needed in the theoretical models used for the interpretation of high "overtone" vibrational transitions.

Introduction

Recent experiments in chemical kinetics have shown quite clearly that the products of various exothermic reactions are formed in unusual vibrational distributions. Some examples of specific vibrational excitation of product species are furnished by the reaction

$$H + O_3 \longrightarrow OH^* + O_2 \qquad (I)$$

where the OH appears to be formed in levels up to $v = 9$ of the $^2\pi$ ground state[3]; the reaction

$$O + ClO_2 \longrightarrow ClO + O_2^* \qquad (II)$$

where the O_2 in the $^3\Sigma^-$ ground state has been observed with appreciable concentration up to the 8th vibrational level[4]; the reaction

$$O + O_3 \longrightarrow O_2 + O_2^* \qquad (III)$$

where excitation of the 13th to 16th vibrational levels of oxygen is found[5]; and the termolecular reaction discussed by Herzberg[6] where the C_2

$$C + C + M \longrightarrow C_2^* + M \qquad (IV)$$

appears to be formed in the 6th vibrational level of the electronically excited $^3\pi_g$ state.

The mode of formation and the subsequent radiative and collisional deactivation of these excited species poses some interesting problems in the fields of reaction kinetics and intermolecular energy exchange. The experiments to date have been qualitative, in the sense that they have identified the phenomenon but have not provided sufficient data for quantitative evaluation of the problems of the number of molecules formed in specific levels and the efficiency of collisional transfer of vibrational energy. The most successful attempt to date to treat the former is that of Heaps and Herzberg[7] on Meinel's data for reaction I as it occurs in the night sky.[8]

In order to provide a basis for further theoretical work in these fields we have undertaken a reinvestigation of reaction I under laboratory conditions with the object of determining the dipole moment parameters and the vibrational population distribution in the OH product molecules produced in these high vibrational levels. This study complements the recent report by Kraus[9] on the rotational population in this system. While definitive answers concerning some of the problems have not yet been obtained, considerable information which sheds light on the molecular mechanics of this reaction has accumulated and is presented here.

Experimental

The radiation was produced by mixing a stream of ozon-

---

[1] Supported by the U. S. Air Force under Contract No. AF-18-(600)-134 (with Princeton University) and No. CSO 680-56-30 (with the National Bureau of Standards). AFOSR TN-58-1076, AD No. 207455.

[2] Presented at the 131st meeting of the American Chemical Society, Miami, Florida, April, 1957.

[3] J. D. McKinley, D. Garvin and M. J. Boudart, *J. Chem. Phys.*, **23**, 784 (1955).

[4] F. J. Lipscomb, R. G. W. Norrish and B. A. Thrush, *Proc. Roy. Soc.* (*London*), **233A**, 455 (1956).

[5] W. D. McGrath and R. G. W. Norrish, *ibid.*, **242A**, 265 (1957).

[6] G. Herzberg, *Astrophys. J.*, **89**, 290 (1939).

[7] H. S. Heaps and G. Herzberg, *Z. Physik*, **133**, 48 (1952).

[8] A. B. Meinel, *Astrophys. J.*, **111**, 555; **112**, 120 (1950).

[9] F. Kraus, *Z. Naturforsch.*, **12A**, 479 (1957).

ized oxygen into a slowly moving, low pressure (4.0 ± 0.1 mm.) atmosphere of H_2 containing an excess of hydrogen atoms. Timed spectrographic exposures of the flame and of a wolfram strip lamp were taken. These, along with certain ancillary data, formed the basis of the calculation of OH line intensities given here. Details of the experimental procedure are given.

1. **Production of the Radiation.**—The method was similar to that used by Ferguson and Broida[10] for "atomic flames" and by McKinley[3] in earlier work on this system. Oxygen (from the reduction of air), purified by passage through heated magnesium oxide and a carbon dioxide–water absorption chain, was ozonized (about 3% ozone) in a Welsbach T-23 Ozonator. This mixture was metered, then passed through a slot-shaped nozzle into the Pyrex reactor. Hydrogen, metered, then passed through a water bubbler, was partially atomized in a conventional low pressure electrode discharge (Wood's tube) and fed into the reactor *via* a wide tube concentric with and longer than the nozzle. The reactor geometry, nozzle shape and the relative gas flows (oxygen = 60, hydrogen = 4 millimoles/min.) restricted the luminous reaction to a narrow region extending out from the nozzle face toward the plane quartz window. Viewed end on, this formed a reasonably uniform line source for spectroscopy. Reactor pressures were determined to 0.2 mm. on a Bourdon gauge.

In contrast to the previous work on this system, in which concentrated ozone was employed, ozonized oxygen has been used here thus eliminating a major experimental hazard. In spite of this the ozone flow rates here are greater than those used before. This was possible only by using a very high capacity vacuum system (based on a Stokes Microvac Pump). The reacted gases (principally a H_2–O_2 mixture) could be pumped without danger provided ozone did not reach the pump fluid. Destruction of ozone by the excess H atoms in the reaction mixture proved to be a more satisfactory safety precaution than the use of heated tubes or silver screening.

2. **Spectroscopy.**—All spectra were taken on an f/0.8 Auroral Spectrograph similar to that described by Petrie.[11] In this instrument the light, filtered at the entrance slit to eliminate overlapping orders and masked at will by a five step Hartmann diaphragm, is deflected by a plane mirror onto an f/4 parabolic reflector, and then, in a parallel beam, is cast almost normally onto a 4 × 5 in. Bausch and Lomb 15,000 line/inch grating. The diffracted radiation is observed with a quartz f/0.8 Schmidt flat-field camera. The first-order dispersion is about 135 Å./mm. and varies slightly with wave length. About 1800 Å. may be recorded at a time. The high speed of this spectrograph makes it ideal for the study of weak sources.

The flame radiation was focused onto the entrance slit by a 65 mm. focal length f/1.1 quartz doublet lens with a 1:1.67 magnification (which was then reduced 5-fold by the spectrograph). Several timed exposures were made on each plate using the Hartmann diaphragm. Neon, argon or mercury reference lines were also placed on each of these plates and those described below. A slit width of 150 μ was used for all plates in order to provide wide lines suitable for photometry.

Similar length exposures of a wolfram strip lamp were made on separate plates immediately following the flame exposures. The wolfram lamp operated from a stabilized direct current source, its apparent temperature being checked during exposure by a calibrated Leeds and Northrup portable optical pyrometer. The lamp temperature was maintained near 1500°, the maximum variation during an exposure being 25°. The immediate source of the W radiation for the spectrograph was a chalk reflector placed 10 cm. in front of the entrance slit and 26 cm. from the lamp. The radiation, chopped by a variable aperture sector, thus provided a source weak enough for comparison with the flame plates but still retaining sufficient aperture to fill the grating.

3. **Photography.**—Eastman Kodak Company Spectrographic Plates types 103-a O, B and F, and I-N, M and Z were used in their optimum ranges. The last two were hypersensitized with ammonia before use. Corresponding flame and wolfram lamp plates were cut from the same stock and processed together. All plates were developed for four minutes in D-19 and dried in the usual manner. The series of plates used for intensity measurements was taken within a period of 48 hr.

4. **Determination of Spectral Intensities.**—It was assumed that the interpretation of plate blackening caused by the line-source OH flame, under wide-slit conditions, can be based upon the plate blackening-wolfram lamp continuum relationships that obtain under the same spectrographic conditions.

For the latter the relative exposures were determined as follows. Apparent average lamp temperatures were corrected for the emissivity of wolfram at the pyrometer wave length (6500 Å.). The relative energy output then was calculated using tabulated values of the Planck radiation function[12] and of wolfram emissivity[13] and the measured exposure times. Charts of plate optical density *versus* log exposure (as a function of wave length) were prepared and used to interpret the blackening on the flame plates in terms of the energy of the source. Usually two or three exposures were available for each line on each plate; from these the average value of the intensity of the line was determined and recorded. All intensities were normalized to the same base, the plates being interrelated by equating the intensities of lines observed on overlapping pairs of plates.

All plate density measurements were made on Leeds and Northrup Recording Microdensitometers. The calculated exposures and intensities were corected for the transmission and reflection characteristics of the optical components between the lamp (or flame) and the spectrograph.

Although the precautions needed for precision photographic spectrography were taken as indicated above, most of them (except the W emissivity correction) produced minor modifications in the data. Analysis of the final data shows that our precision is not high, a result to be expected from the weak nature of the source, the long exposures and the extended calculations. Probably the major source of systematic error in this work, and one that is difficult to evaluate, comes from the intercomparison of lines in different bands photographed on different plates. When, as explained below, relative band intensities were determined, the fractional errors in these ranged from 0.06 to 0.22 and averaged 0.10. The consistencies that appeared in the processing of these data suggest that such errors give a fair estimate of the precision here.

Results

The radiation, surveyed from 3900 to 11,300 Å., consisted of a spectrum of overlapping bands which can be assigned to vibrational–rotational transitions of hydroxyl in its electronic ground state ($^2\pi$) by comparison with frequencies calculated from energy levels. All bands originating in upper levels with $v \leqq 9$ occurring in this region were found. In addition, a few lines in the 10–3 and 10–4 bands were identified. Only one unidentified feature, a triple headed band near 3970 Å., was observed. This may be assigned neither to hydroxyl nor oxygen.

The major characteristics of this spectrum (Fig. 1) are as follows. Bands with the same Δv lie in the same region, those with higher upper states being at longer wave lengths. Within each sequence the apparent intensity increases with the upper state (except that bands originating in $v = 10$ are weaker than those from $v = 9$). Each band shows R, Q and P branches. At the dispersions used here little structure was observed in the R and Q branches but the P branch lines were well resolved into spin (but not lambda) doublets. As expected the higher frequency component of each

---

[10] R. E. Ferguson and H. P. Broida, "Fifth Symposium (International) on Combustion, Pittsburgh, 1954," Reinhold Publ. Corp., New York, N. Y., 1955, p. 754.

[11] W. Petrie and R. Small, *Astrophys. J.*, **116**, 433 (1952).

[12] E. Jahnke and F. Emde, "Table of Functions," 4th Ed., Dover Publ. Co., New York, N. Y., 1945, Addenda p. 46.

[13] J. C. DeVos, *Physica*, **20**, 690 (1954), and "The Emissivity of W, The W Striplamp as a Standard Radiation Source," Doctoral Dissertation, Amsterdam, 1953.

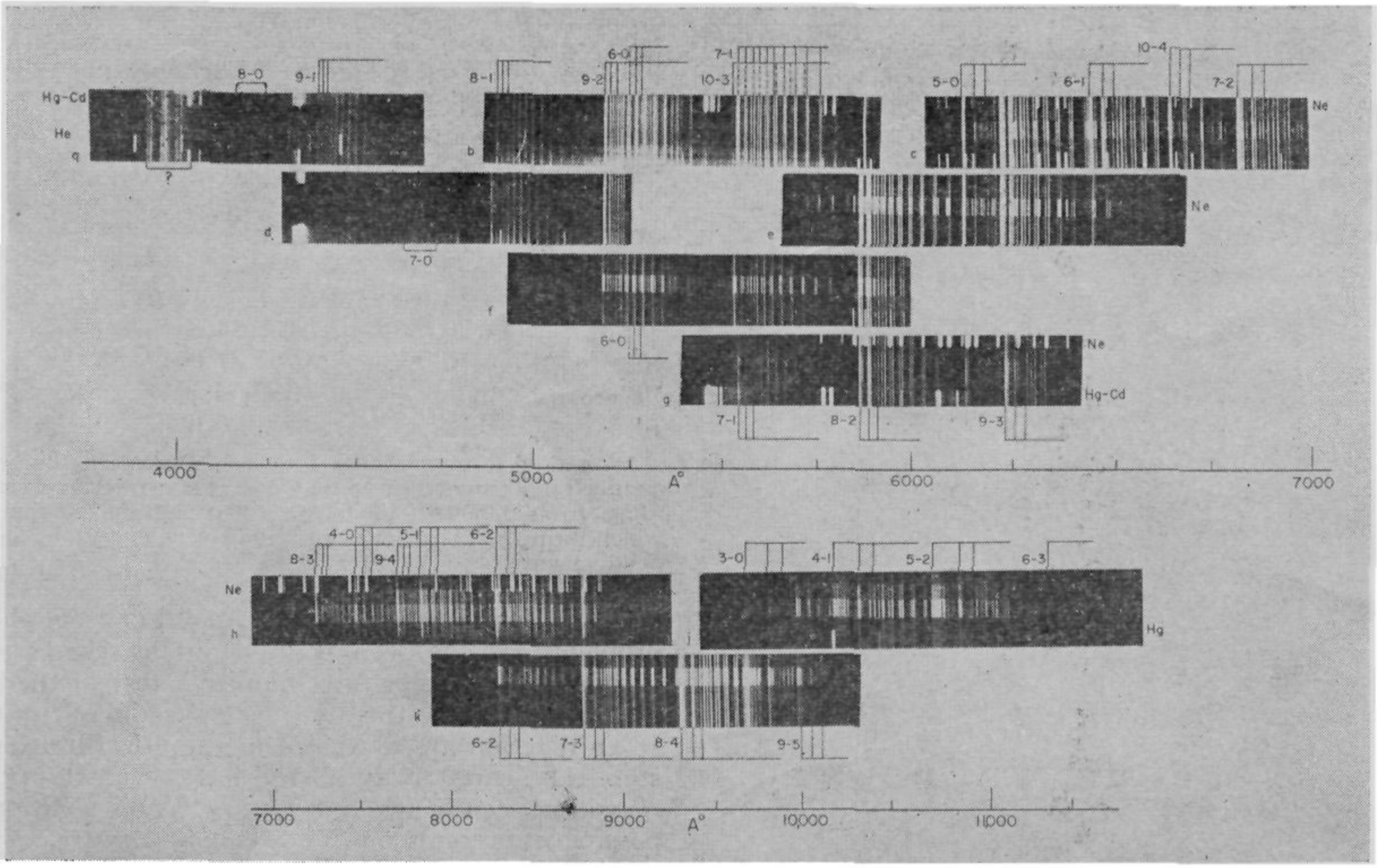

Fig. 1.—Hydroxyl radical spectrum produced in the H + O_3 atomic flame at 4 mm. Plates taken in second order (upper group) and first order (lower group) of f/0.8 Auroral Spectrograph. Bands identified by R and Q head position and average of the first P branch doublet. Radiation focussed on 150 μ spectrograph slit with quartz doublet lens except as indicated below. Plate conditions (l to r): (a) 103aO type plate 67 min. exposure. Faint lines of the 8–0 band appear in the middle of the plate. The unidentified, "three headed" band heads at 3921, 3962 and 4005 Å. The three intense sharp lines are 3934, 3973 and 4018 Å. (Ca ?). (b) 103aB, 35 min. Distinct but weak lines of the 10–3 band appear. (c) 103aF, 10.4 and 21.6 min. Faint 10–4 band lines. (d) 103aB, 43 min. Weak 7–0 band P and Q lines in middle of plate. (e) 103aB, 20 and 44 min. (f) 103aB, 14 and 43 min. (g) 103aB, 50 μ slit, no focussing lens, 85 min. (h) I–N, 50 μ slit, no focussing lens, 10, 20, 40 and 80 min. (j) I–Z hypersensitized, 11.7, 24, 47.2 min. (k) I–M hypersensitized, 10 and 33.7 min.

doublet is the weaker. The intensity maximum for each band lies at K = 4 or 5.

The lines for which intensity measurements have been made are given in Table I. The line designations follow Dieke and Crosswhite.[14] Many lines apparent in Fig. 1 are not reported in the table. These either were overlapped, the doublets were not separated or the intensities fell outside the feasible range of plate calibration. Line frequencies in the P branches are in good agreement with those calculated from previous work[14–16] and are not given here.

Using the principle explained below an approximate measure of the relative (photon) intensities of the vibrational bands has been calculated and is given in Table II. In general the intensity of an emission line depends upon the population in the upper state, $N(v,K)$ and the transition probability $f = f(v,\Delta v;K)$. If the rotational line strengths (transition probabilities), $S(K)$, are independent of the vibrational transition, then the ratio of intensities of two lines in different bands but with the same rotational upper state is

$$\frac{N(v,K)f(v,\Delta v;\ K)}{N(v',K)f(v'\Delta v;\ K)} = \frac{N(v)f(v,\Delta v)S(K)}{N(v')f(v',\Delta v)S(K)} = \frac{N(v)f(v,\Delta v)}{N(v')f(v',\Delta v)} \quad (1)$$

where v and v′ represent different upper vibrational states.

The relative intensities for all such pairs of lines in a particular band pair were calculated and averaged to give the relative band intensities. From the latter an internally consistent set of relative $N(v)f(v,\Delta v)$ values was prepared using the 8–3 band as the arbitrary base. Relative values of $f(v,\Delta v)$ for transitions from the same upper level may be read directly from Table II. Other comparisons require specific assumptions concerning the populations of the levels.

The recent work of Herman, Rothery and Rubin[17] indicates that this method of averaging the intensity ratios should introduce some bias. However, examination of our data does not reveal the predicted trend, which may well be below the level of our experimental errors.

Derived Results and Discussion

The existence of an extended set of intensity data for OH should permit the determination of some molecular parameters and estimation of the molecu-

---

(14) G. H. Dieke and H. M. Crosswhite, "The Ultra-Violet Bands of OH: Fundamental Data," ("Bumblebee Series," Report No. 87 [The Johns Hopkins University, 1948]).

(15) R. C. Herman and G. A. Hornbeck, *Astrophys. J.*, **118**, 214 (1953).

(16) T. M. Cawthon, Jr., and J. D. McKinley, Jr., *J. Chem. Phys.*, **25**, 585 (1956).

(17) R. Herman, R. W. Rothery and R. J. Rubin, *J. Molec. Spec.*, **2**, 369 (1958).

TABLE I: INTENSITIES OF OH($^2\pi$) VIBRATIONAL-ROTATIONAL TRANSITIONS

$(I/\nu^4) = Nf$ in arbitrary units. ($P_2(3)$ = P branch, $K = 3$ in lower state, spin component 2). Experimental conditions: 4 mm. Hg, approximate gas flows: $O_2 = 58$, $O_3 = 2$, $H_2 = 40$ millimoles/sec.

	Bands:																				
Line designation	9-2 B[a]	9-3 C	9-4 D	9-5 F	8-2 B	8-3 D	8-4 E	7-1 A	7-2 C, D	7-3 E	6-0 A	6-1 B, C	6-2 D, E	5-0 B	5-1 D	5-2 F	4-0 D	4-1 F	3-0 E, F	10-3 A	10-4 C
$P_2(2)$	0.021					2.2	106		0.78	68		0.21	8.0		2.75	560	0.73	660	220		
$P_1(2)$			5.31	272	0.38	4.4	169		1.50	76			19.2	0.11		1110		910	275		0.0585
$P_2(3)$	.040		4.10	190	.32	4.2	153		1.20	135	0.016	.40	14.4	.096		1040	1.05	740	380		
$P_1(3)$		1.06	10.1		.68	8.4	244		2.5	88	.029	.96		.21	11.5	1800	3.0	1170			.0585
$P_2(4)$	.053					5.0	171	0.084	1.74	129		.42	14			1080		900			.102
$P_1(4)$						10.9	260		3.1	80	.030	.78	(60)			1840		1240			
$P_2(5)$		0.57			.42	5.8	176	.102	1.63	137		.54	30		6.1	1180	1.5	930		0.0098	.075
$P_1(5)$					.81	9.1	253		2.8			.68	(56)		12.4	1620	2.6	1170			
$P_2(6)$		.51			.33		168	.071		111	.014	.44	(32)			730		640		.0089	
$P_1(6)$		.92			.58		226		2.2		.023		(47)		8.35	1430	1.8	852			
$P_2(7)$	$.037_7$	.31			.30			.067			$.008_7$		21							.0068	
$P_1(7)$		.53			.43			.108	1.42		.011		42							.0045	
$P_2(8)$		$.16_5$			.17			.042				.24	23							.0045	
$P_1(8)$		.27			.23			.063				.35	30								
$P_2(9)$	.018							.032					13								
$P_1(9)$	.020							.042													
$P_2(10)$								.021													
$P_1(10)$								.029													

[a] Spectrographic plate designation.

TABLE II

RELATIVE INTENSITIES OF OH VIBRATIONAL BANDS EMITTED IN THE SYSTEM[a] $H + O_3 \longrightarrow OH^* + O_2$

$$I/\nu^4 = N_{v'}f_{vv'}$$

v' =	0	1	2	3	4	5
3	46.4	.....				
4	0.278	154	.....			
5	0.0211	1.20	205			
6	0.0044	0.0995	5.39			
7	.....	0.0218	0.309	14.8		
8		.....	0.0767	1.00	32.0	
9			0.0130	0.104	1.08	47.9
10				0.0012	0.011	

[a] Based on P branch lines, rotational line strengths being assumed independent of v and v'. Average fractional errors range from 0.05 to 0.20 for ratios of the above numbers which form the "best set" of twenty over-determined independent variables.

lar population distribution. Solution of these problems, as has been pointed out by Heaps and Herzberg,[7] underlies any definitive test of the hypothesis that all the hydroxyls produced in the $H-O_3$ reaction are produced in the 9th vibrational state, *i.e.*, carry away all the heat of reaction.[18,19] As will be seen below, only a very limited solution is possible at present.

a. Rotational and Spin-Doublet Populations within Individual Vibrational Levels.—Meinel[8] and Kraus[9] have developed the analysis of this system in these respects and have reported rotational and doublet temperatures for their night sky and laboratory data. In this procedure, the observed line intensities, corrected for the intrinsic line strengths (rotational transition probabilities) are used to characterize a Boltzmann distribution of molecules in the various rotational and doublet energy levels. Kraus' calculations give T_{rot} = 700°K. (laboratory) and 200°K. (night sky), and T_{rot}/T_{doub} = 1.4 to 1.7.

Our results do not agree with these estimates, and indeed suggest that either there are several Boltzmann distributions or that it is incorrect to assign either of these temperatures. The crux of the matter is that the choice of values for the line strengths for OH materially affects the results. Sets of line strengths based on OH being intermediate between Hund's coupling cases a and b have been given by Benedict, Plyler and Humphreys[20] and by Kraus. These approach each other at high rotational quantum numbers (K) but differ markedly at low values. In contrast to the combustion flames studied by the former authors, the low K lines are more important in this atomic flame. To illustrate this, the marked upward curvature in Kraus' rotational analysis plots (his Fig. 6) is due in large part to the choice of line strength.

We have employed Benedict's values, since many doublet intensity ratios in both sets of laboratory data are less than the minima required by the other set. Rotational temperatures have been assigned,

---

(18) D. R. Bates and M. Nicolet, *Pub. Astron. Soc. Rec.*, **62**, 106 (1950).

(19) G. Herzberg, *J. Roy. Astron. Soc. Canada*, **45**, 100 (1951).

(20) W. S. Benedict, E. K. Plyler and C. J. Humphreys, *J. Chem. Phys.*, **21**, 398 (1953).

treating the doublet components separately. For the data in Table I, the stronger doublet components yield $T_{rot} = 470 \pm 70°$K. (average deviation) and a range from 330 to 640°K. in 13 bands. The weaker components give $T_{rot} = 610 \pm 90°$K. with a range from 415 to 815°K. (11 bands). Usually there is appreciable scatter in the points within a band, and the line with K = 2 has been ignored. No trends in T_{rot} with upper state or Δv were observed.

Kraus' data (his Table II) combined with Benedict's line strengths showed the same temperature for both branches of the doublet structure, an average of 790 ± 110°K. (6 bands) with a range from 625 to 1020°K. Here too a random variation of temperature from band to band occurs and the fit of the points within a band to the model is mediocre.

Spin doublet intensity ratios also lead to different temperatures for the two sets of data. In general these ratios are greater in our experiments than in Kraus' and hence lead to lower temperature estimates. But, for both sets of data, the most characteristic result is the lack of constancy in the temperatures estimated for the doublets within each vibrational band. Part of this is due to magnification of small errors in the calculation, but its prevalence and magnitude lead us to question the relevance of these and earlier estimates. (An average of band averages for Kraus' data gave T_{doub} = 1300°K. and for ours 310°K.) No significant correlation of the band by band doublet and rotational temperatures was noted.

Apart from these internal inconsistencies, the comparison of the two sets of laboratory data show major deviations. We believe that this is largely due to the mode of production of the radiation and the environment in which it is observed. In some photometric studies of this system in the wave length region 1.5 to 3.0 μ (to be reported separately) the intensity distributions within bands and from band to band varied markedly with pressure, mixture ratio and the method of producing the hydrogen atoms. Thus, variant results in spin-doublet and rotational populations are to be expected in the laboratory studies.

b. Vibrational Transition Probabilities and the Dipole Moment of OH.—Heaps and Herzberg[7] have presented the treatment of this problem in some detail, considering the transition moments based on the Morse oscillator wave functions and a series expansion of the dipole moment as a function of internuclear distance

$$M = M_0 + M_2(r - re) + M_2(r - re)^2 + M_3(r - re)^3 + \quad (2)$$

They employed the quadratic form and estimated M_2/M_1 for OH from the night sky data. With our more extensive data we find systematic variations in this constant as a function of Δv and the particular vibrational levels in the transition.

We have checked their treatment of the moments by the use of Infeld and Hull's Factorization Method and have determined the integrals for the cubic term of the power series.[21,22] These moment integrals are summarized in the Appendix and their values for OH are given in Table III. (The values for the linear and quadratic moment

TABLE III

VIBRATIONAL TRANSITION MOMENT INTEGRALS FOR OH ($k = 39.57$) AS A NON-ROTATING MORSE OSCILLATOR

$_1Ivv'$ (eq. 6): First moment integral

v =	0	1	2	3	4	5	6	
v′ = 1	−0.1614	.....						
2	−0.0186	−0.231	.....					
3	-3.53×10^{-3}	−0.0331	−0.287	.....				
4	-8.82×10^{-4}	-7.35×10^{-3}	− .0478	−0.333	.....			
5	-2.68×10^{-4}	-2.092×10^{-3}	− .0121	− .0636	.....	.....		
6	-9.36×10^{-5}	-7.07×10^{-4}	-3.84×10^{-3}	− .0179	−0.0806	.....	.....	
7	-3.70×10^{-5}	-2.70×10^{-4}	-1.41×10^{-3}	-6.18×10^{-3}	−0.0246	−0.0974	.....	
8	-1.622×10^{-5}	-1.156×10^{-4}	-5.90×10^{-4}	-2.475×10^{-3}	-9.32×10^{-3}	− .0328	−0.117	.....
9	.....	.....	-2.94×10^{-4}	-1.207×10^{-3}	-4.35×10^{-3}	− .0141	−0.0457	−0.1360

$(t_2 - \ln k)$, (eq. 7) partial second moment integral

v =	0	1	2	3	4	5	6	
v′ = 1	−0.051	.....						
2	+0.908	−0.135	.....					
3	1.376	+0.847	−0.209	.....				
4	1.698	1.312	+0.782	−0.286	.....			
5	1.905	1.615	1.245	+0.696	−0.374	.....		
6	2.072	1.838	1.548	1.168	+0.612	−0.470	.....	
7	2.210	2.015	1.764	1.469	1.085	+0.520	.....	.....
8	2.312	2.138	1.926	1.685	1.386	0.998	+0.424	.....
9	2.410	2.251	2.065	1.850	1.605	1.298	0.910	+0.317

$(t_3 - (\ln k)^2)$, (eq. 8) partial third moment integral

v =	0	1	2	3	4	5	6	
v′ = 1	−0.45	.....						
2	+6.53	−0.87	.....					
3	10.83	+6.00	−1.41	.....				
4	13.90	10.18	+5.34	−1.91				
5	16.21	13.22	9.49	.....				
6	18.16	15.70	12.48	.....				
7	19.70	17.45	14.79	+11.64				
8	20.99	.....	16.53	13.86	+10.83			
9			18.06	15.72	12.97	+9.94		

---

[21] D. Garvin, "Transition Probabilities for the Morse Oscillator with a Cubic Dipole Moment" (AFOSR TN 58 146, AD No. 152173), Princeton University, 1958.

[22] L. Infeld and T. E. Hull, *Rev. Mod. Phys.*, **23**, 21 (1951).

integrals agree well with those of Heaps and Herzberg, except that the signs before all their quadratic moments are reversed. This unfortunate error led them to report negative values for M_2/M_1.)

Using the method explained in the Appendix (see eq. 9), the $Nf_{vv'}$ values (Table II) for 11 pairs of contiguous bands and the moment integrals (Table III), values for M_2/M_1 and M_3/M_1 were obtained. Two sets of results occur, depending upon the choice of the sign before the square root in equation 9. Both are given in Table IV along with our calculations for Meinel's night sky intensities. Not only are the laboratory and night sky results consistent, but the + and − sets are identical within experimental error.

TABLE IV

DIPOLE MOMENT CONSTANTS[a]

	This work	Night sky
$M_2/\beta M_2$	−: +0.40 ± 0.08	+0.40
	+: + .37 ± .05	+ .38
$M_3/\beta^2 M_1$	−: + .076 ± 0.005	+ .074
	+: + .068 ± .003	+ .068

[a] $\beta = 2.32 \times 10^8$ (Morse curve parameter).

Since the sign and magnitude of M_1 and its relation of M_0 are unknown, the conclusion that may be drawn from the relative magnitudes of M_2 and M_1 is that, in the region of interest, the dipole moment is either rising or falling *very sharply* with changes in internuclear distance.

Although the results in Table IV are encouraging in the sense that a large body of intensity data is self consistent, they are not of use, unfortunately, in the solution of the vibrational level population problem. When vibrational transition probabilities (eq. 5. Appendix) are calculated from the dipole moment parameters and the integrals in Table III, most of these differ from zero by less than the experimental error and do not reproduce the input intensity data with any accuracy. Failing this test, any estimate of the level populations would be speculation.

The origin of this difficulty may be found by comparing the Nf_v's in Table II and the linear moment integrals, ${}_1I_{vv'}$ in Table III. If ratios of intensities for bands originating in the same level, *viz.* 9–4/9–3, 9–3/9–2, etc., are compared with the corresponding values of ratios of ${}_1I_{vv'}$, the former are seen to *decrease* as *v* decreases while the latter *increase*. Thus, in the application of equation 9 (Appendix) constants that reverse the trend in the dominant term are obtained. Under these conditions accurate reproduction of input data of limited precision is difficult to achieve.

This situation again suggests that, as in the case of the rotational temperature determination, the model employed in the interpretation of the vibrational band intensities is not suitable. Although the "Morse potential-series dipole moment" model has proved to be very good for interpreting accurate HCl and DCl intensity data[23] the applicability to higher level transitions may be poor. It is known that several anharmonicity terms are needed to represent the potential for OH.[24] While these terms produce only small changes in energy levels from the levels predicted by the Morse potential treatment, the changes in the transition moment integrals could be appreciable. Unfortunately, no more refined treatment is currently available.

Another source of error may lie in the assumption of a limited power series representation of the dipole moment. Mecke[25] has discussed this and elsewhere we have developed a generalization of his treatment of the Morse oscillator with an exponentially decaying dipole moment.[26] Such a treatment is intuitively attractive and permits the correlation of intensity data without requiring as many adjustable parameters as needed in the series-dipole case. However, its applicability to the present case remains doubtful until it has been tested on more accurate intensity data. In summary, it appears that an appreciable further theoretical development of models for the interpretation of vibrational band intensities in diatomic molecules must precede the detailed interpretation of high Δv intensity data.

Acknowledgments.—The author is indebted to the National Bureau of Standards for a Visiting Fellowship during the summer of 1956 when the experiments were carried out. Discussions with Drs. H. P. Broida and K. E. Shuler were invaluable in the development of this work. Drs. A. M. Bass and H. J. Kostkowski guided him in matters relating to their special fields. The generous loan of the Auroral Spectrograph by the Air Force Geophysics Research Directorate, Boston, Massachusetts, made possible the measurements. Microdensitometers were made available to us at the National Bureau of Standards and the David Sarnoff Research Center, Radio Corporation of America, Princeton. Extensive calculations were made by Messrs. Wm. B. Mather, Jr., and C. William Jansing. To all of these we express our appreciation.

Appendix

When a power series dipole moment (eq. 2, see text) and the Morse potential

$$U(u) = D_e(1 - \exp(-\beta u))^2 \qquad (3)$$

where $u = r - re$, D_e the dissociation energy and $\beta = \omega_e\sqrt{2\pi^2 c\mu/D_e h}$ are assumed for a diatomic molecule, the vibrational transition moment integral for the non-rotating Morse oscillator may be written

$$f_{vv'} = \int \psi_{v'} M(u)\, \psi_v \, du \qquad v < v' \qquad (4)$$

Equation 4 solved by the factorization method, and retaining terms through u^3 in eq 2, becomes

$$f_{vv'} = {}_1I_{vv'}\,[-M_1/\beta - 2M_2 \ln k/\beta - 3M_3(\ln k)^2/\beta^3] + {}_2I_{vv'}\,[M_2/\beta^2 + 3M_3 \ln k/\beta^3] - {}_3I_{vv'}\,M_3/\beta^3$$

where, following the notation of Infeld and Hull

---

(23) W. S. Benedict, R. Herman, G. E. Moore and S. Silverman, *J. Chem. Phys.*, **26**, 1671 (1957).

(24) G. A. Hornbeck, "Fifth Symposium (International) on Combustion, Pittsburgh, 1954," Reinhold Publ. Corp., New York, N. Y., 1955, p. 790.

(25) R. Mecke, *Z. Naturforsch.*, **54**, 38 (1950).

(26) D. Garvin, "Transition Probabilities for the Rotating Morse Oscillator with an Exponential Dipole Moment" (AFOSR TN 58-95 AD No. 148144) Princeton University, 1958; copies may be obtained by writing to the author. Also, see ref. 17.

$$ {}_1I_{vv'} = \int U_m{}^s\, x\, U_{m'}{}^s\, dx $$
$$ {}_2I_{vv'} = \int U_m{}^s\, x^2\, U_{m'}{}^s\, dx = 2\,{}_1I_{vv'} \cdot t_2 $$
$$ {}_3I_{vv'} = \int U_m{}^s\, x^3\, U_{m'}{}^s\, dx = 3\,{}_1I_{vv'} \cdot t_3 $$

Thus

$$ f_{vv'} = = -(M_1/\beta)\,{}_1I_{vv'}\left[1 - 2\left(\frac{M_2}{\beta M_1} + \frac{3M_3 \ln k}{\beta^2 M_1}\right)(t_2 - \ln k) + \frac{3M_3}{\beta^2 M_2}(t_3 - (\ln k)^2)\right] \quad (5) $$

The three functions ${}_1I_{vv'}$, $(t_2 - \ln k)$ and $(t_3 - (\ln k)^2)$ are defined below and are those listed in Table III. The parameter $k = 1/xe$ is the anharmonicity constant for the molecule.

$$ {}_1I_{vv'} = \frac{1}{(v' - v)(k - v' - v - 1)} \times \left[\frac{v'!\,(k - v' - 1)!(k - 2v - 1)(k - 2v' - 1)}{v!(k - v - 1)!}\right]^{1/2} = \beta r_e S_1{}^{vv'} \quad (6) $$

where S_1 is given by equation 50, reference 7.

$$ (t_2 - \ln k) = \psi\,(k - v - v' - 1) - \ln k + \sum_{j=0}^{j=v'-v-2} \frac{1}{1+j} - \sum_{K=0}^{K=v-1} \frac{K!\,(k - 2v - 1 + K)!}{(v' - v + 1 + K)!(k - v - v' + K)!} \times \sum_{i=0}^{i=K} \frac{(v' - v + i)!(k - v' - v - 1 + i)!}{i!(k - 2v - 1 + i)!} = \frac{1}{r_e}\cdot\frac{S_{II}}{S_I} \quad (7) $$

where S_{II} is defined by eq. 51 in reference 7. For all practical purposes, although simple formulas for it exist, the double sum may be approximated by

$$ \Sigma\,\Sigma = v/(v' - v + 1)(k - v' - v) \equiv vA_{vv'} $$

and this has been done in Table III.

$$ t_3 - (\ln k)^2 = \psi^2(k - v' - v - 1) + \psi'(k - v' - v - 1) - (\ln k)^2 + 2\sum_{i=0}^{i=v'-v-2} \frac{1}{1+i}\left(\psi(k - v' - v - 1) + \sum_{j=0}^{=v'-v-3-i} \frac{1}{2+i+j}\right) + 2\left(1 - \psi\,(k - v' - v - 1) - \sum_{i=0}^{i=v'-v-2} \frac{1}{1+i}\right)vA_{vv'} \quad (8) $$

where a similar approximation has been made and a quadruple sum of the order of $vA_{vv'}{}^2$ has been dropped. In these equations $\psi(\alpha)$ is the logarithmic derivative of the gamma function, for which $\psi(\alpha) = (\alpha - 1)!$ if α is an integer. $\psi'(\alpha) = d\psi/d\alpha$.

The dipole constants then are determined from the formula

$$ \pm\left[\frac{(I/\nu^4)_a}{(I/\nu^4)_b}\right]^{1/2} = \frac{(f_{vv'})_a}{(f_{vv''})_b} \quad (9) $$

in which only the parameters given in Table IV occur (a and b are two bands originating in the same upper level).

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

Iodine Nuclear Quadrupole Resonance Spectrum of Boron Triiodide[1]

BY W. G. LAURITA AND W. S. KOSKI

RECEIVED JANUARY 8, 1959

The iodine nuclear quadrupole resonance spectrum of boron triiodide has been studied. The frequencies of the $^1/_2 \rightarrow {}^3/_2$ and the $^3/_2 \rightarrow {}^5/_2$ transitions were measured as 212.6 and 340.1 Mc./sec., respectively. Each of the resonances was a doublet with a separation of 25 kc./sec. for the lower frequency transition and an approximate intensity ratio of 1 to 4. The quadrupole coupling constant (eQq) was found to be 1176 Mc./sec. and the asymmetry parameter was 0.456. The large asymmetry parameter was interpreted as due to π-bond character of the boron–iodine bond. The experimental data are discussed in terms of significance to the electronic structure of the molecule. The number of iodine resonances in boron triiodide was found to be the same as the number of resonances found in other boron trihalides for corresponding transitions. This suggests that the crystal structure of BI_3 is the same as BBr_3 and BCl_3 which are known.

Introduction

Nuclei such as I^{127}, which have an asymmetrical distribution of charge, possess a quadrupole moment. Such nuclei interact with the electrons and other nuclei in a molecule or a crystal to produce a variation in the electrostatic energy of the system with nuclear orientation. Transitions between these orientational energy levels give rise to hyperfine structure in the rotational spectra of molecules and to the so-called pure nuclear quadrupole spectra in solids. The energy of the electrostatic interaction between the asymmetric nuclei and the electric field of the molecule or crystal depends on the nuclear quadrupole moment (Q), on the nuclear spin (I) and on the second derivative of the potential relative to the appropriate axes. The z-axis is considered to be the bond axis and $q_{zz} = \partial^2 V/\partial z^2$, $q_{yy} = \partial^2 V/\partial y^2$ and $q_{xx} = \partial^2 V/\partial x^2$. The experimental data permit an evaluation of eQq_{zz}, the quadrupole coupling constant in which e is the proton charge and an asymmetry parameter (η).

$$ \eta = \frac{q_{xx} - q_{yy}}{q_{zz}} $$

These two quantities are intimately related to the distribution of electronic charge in the molecule and have been interpreted in a semi-empirical fashion in terms of electronic structure of molecules.

---

[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600)-1526. Reproduction in whole or in part is permitted for any purpose of the United States Government.