JULY 15, 1935 PHYSICAL REVIEW VOLUME 48

The Spectrum of AgD

PHILIP G. KOONTZ,* *Sloane Physics Laboratory, Yale University*

(Received April 29, 1935)

The spectrum of AgD has been photographed at high dispersion with an Ag arc in an atmosphere of deuterium as a source. Quantum analyses of the 0,0 and 1,1 bands are presented. The value $B_e = 3.2595$ is found for the lower state. Comparing this with the corresponding value for AgH, the ratio B_e^i/B_e for the two isotopic molecules is 0.50511, whereas the ratio of the reduced masses, by using Aston's latest values for the masses of the H and D atoms, is 0.50497. Calculation of the corrections to B_e for the anharmonic oscillator as given by J. L. Dunham shows them to affect the B_e ratio inappreciably.

INTRODUCTION

RECENT investigations of the spectra of AlD[1] and CaD[2] have stimulated considerable interest in an accurate comparison of the spectra of hydrides with those of the corresponding deuterides. Because of the large differences in the spectra of the two isotopic molecules, the validity of the isotope theory can be determined to a high degree of accuracy. The above investigations have shown that, in certain cases at least, an appreciable discrepancy exists between the values of ρ^2 and the ratio of the rotational constant B_e for the nonrotating, vibrationless isotopic molecules, whereas simple theory predicts their equality. Two different views[1, 3] of the explanation of this discrepancy have developed and it is desirable to obtain additional data from other molecules. The results of an analysis of the spectrum of AgD are here presented.

EXPERIMENTAL PROCEDURE

The $^1\Sigma \rightarrow {}^1\Sigma$ band system of AgH with the system origin near 3300A is well known.[4–8] Spectrograms of the corresponding bands of AgD were taken in the third order of a 21-ft. concave grating in a stigmatic mounting. The dispersion was 1.58A/mm. The light source was a d.c. arc between two silver electrodes, one of which was water-cooled, in an atmosphere of deuterium gas at about 6 cm of Hg pressure. Currents of 5–6 amperes were used. The deuterium gas was obtained from the reaction in a vacuum of a gram of 99 percent deuterium oxide with Ca metal. Of course this reaction liberated only one-half of the deuterium. In this case no attempt was made to recover the remaining half as the CaOD was used as a target in some nuclear disintegration experiments in this laboratory. The AgH bands were present, the H_2 coming from the hot electrodes and electrode mountings, but they were weak and did not cause any difficulties in the analysis.

ROTATIONAL ANALYSIS

The spectrum of AgH may be described as consisting of a few sequences of bands, the spacing of the sequences being much wider than the distance between any adjacent bands forming the sequence. The bands degrade to the red, the R branch forming a head at about $J = 18$. The vibrational part of the isotope theory predicts only a small change toward the violet in the position of the 0,0 band origin of AgD relative to the origin of the corresponding band of AgH, as the difference of the ω_e values for the upper and lower states of AgH is known to be small. The rotational isotope effect predicts a change of nearly 2 to 1 in spacing of the individual lines of the P and R branches for the two isotopic molecules, the heavier isotope forming the smaller pattern. It is found for the 0,0 band, that both the band origin and the head of the R branch of the AgD band lie in the interval between the

---

* Portion of a dissertation presented for the degree of Doctor of Philosophy at Yale University.

[1] Holst and Hulthén, Nature **133**, 496 (1934); Nature **133**, 796 (1934); Zeits. f. Physik **90**, 712 (1934).

[2] Watson, Phys. Rev. **47**, 27 (1935).

[3] R. deL. Kronig, Physica **1**, 617 (1934).

[4] Bengtsson and Svensson, Comptes rendus **180**, 274 (1925).

[5] Hulthén and Zumstein, Phys. Rev. **28**, 13 (1926).

[6] Bengtsson and Hulthén, Trans. Faraday Soc. **25**, 752 (1929).

[7] Bengtsson and Olsson, Zeits. f. Physik **72**, 163 (1931).

[8] Bengtsson: Nova Acta Reg. Soc. Sci. Uppsala (IV) **8**, 23 (1932).

TABLE I. *Assignment of frequencies for* $^1\Sigma \rightarrow {}^1\Sigma$ *AgD bands* (*cm*$^{-1}$ *units*).

	0,0		1,1	
	P	*R*	*P*	*R*
1				
2	29897.86	29928.91		
3	890.91	934.70		29807.48
4	883.83	939.60		812.11
5	876.60	944.61	29750.65	816.47
6	868.78	949.27	742.93	820.37
7	860.97	953.83	734.79	823.86
8	852.94	957.86	726.39	827.10
9	844.65	961.86	717.37	829.80
10	836.21	965.44	708.04	832.50
11	827.10	968.62	698.42	834.64
12	818.50	971.72	688.77	836.21
13	809.08	974.80	678.44	837.50
14	799.70	977.31	667.75	838.74
15	789.90	979.46	656.90	838.74
16	779.92	981.37	645.59	838.74
17	769.94	982.79	633.99	838.74
18	759.52	984.07	622.19	837.50
19	749.05	985.93	609.87	836.21
20	738.01	985.93		834.64
21	727.08	985.93	584.09	832.50
22	715.66	985.93	570.85	829.80
23	704.05	985.93	556.83	826.48
24	692.17	984.81	542.69	822.74
25	680.08	983.47	528.00	818.50
26	667.75	981.97	512.99	813.66
27	655.07	979.92	497.43	807.90
28	642.06	977.53	481.44	801.92
29	629.87	974.80	464.93	795.27
30	615.31	971.72	447.95	787.92
31	601.61	967.96	430.58	779.92
32	587.33	963.73	412.38	770.64
33	572.89	959.00	393.72	761.06
34	557.80	953.83	374.39	750.65
35	542.69	948.08	354.24	739.37
36	527.06	941.78	333.83	727.08
37	511.09	934.70	312.57	713.76
38	494.61	927.22	290.45	699.39
39	477.73	919.16	267.30	684.15
40	460.40	909.96	243.65	667.75
41	442.31	900.37	218.92	650.71
42	423.68	889.93	193.32	630.42
43	404.64	878.56	166.13	
44	385.06	866.30	139.07	
45	364.57	852.94	108.40	
46	343.57	838.74		
47	321.51	823.86		

origin and the *R* branch head of the AgH band. Table I gives the assignment of frequencies to the *P* and *R* branches for the 0,0 and 1,1 bands of AgD. The rotational constants B_v and D_v are evaluated in the usual semi-graphical way from the $\Delta_2F(J)$ values. Table II gives the values obtained for AgD. The values of α_e and B_e are determined from the relation $B_v = B_e - \alpha_e(v+1/2)$ when B_0 and B_1 are known. Simple isotope theory predicts that the ratio of the B_e values for the isotopic molecules should be exactly equal to ρ^2, the ratio of the reduced masses. Using Bengtsson's[8] value $B_e = 6.453$ for the ground state of AgH and the value $B_e = 3.2595$, this ratio is 0.50511.[9]

In calculating the value for ρ^2, Casimir[10] has shown that the masses of the electrons in closed shells should be included with the mass of the nucleus (the effect of adding one electron to the silver atom is negligible), but there is some uncertainty about the proper method of including the mass of the electron associated with the hydrogen atom. If we use the atomic weight of silver, 107.880, and Aston's[11] latest values of atomic masses for hydrogen and deuterium, H = 1.0081 and D = 2.0148, we find $\rho^2 = 0.50497$. By assuming all of the electrons associated with the silver and by using values for the proton and deuteron, $\rho^2 = 0.50485$. A comparison shows that the ratio of the *B* values is larger than the first value of ρ^2 by nearly 0.03 percent and that the discrepancy is a little larger in the second case. This difference is small and is in agreement with Kronig's[3] prediction concerning molecules whose united atom (a concept applicable only in the case of hydrides) is in a ^1S state for which $L = 0$. If one assumes Kronig's explanation this discrepancy could be attributed to the interaction of nearby states, the magnitude of which cannot be calculated. The alternative explanation[1, 9] assumes that a few of the outermost electrons are constrained by the nucleus to take part in the rotation and give an additional contribution to the moment of inertia of the molecule. Data

TABLE II. *Rotational constants for AgD.*

LOWER $^1\Sigma$ STATE	UPPER $^1\Sigma$ STATE
$B_0 = 3.2229$	$B_0 = 3.1015$
$B_1 = 3.1497$	$B_1 = 2.9854$
$D = -8.7 \times 10^{-5}$	$D = -10.1 \times 10^{-5}$
$\alpha_e = 0.0732$	
$B_e = 3.2595$	

---

[9] According to L. Hulthén (Nature **135**, 543 (1935)) E. Hulthén and E. Bengtsson Knave have obtained 0.50527 for the ratio of the B_e's for AgH and AgD.

[10] Casimir, Physica **1**, 1073 (1934).

[11] Aston, Nature **135**, 541 (1935).

obtained recently by the writer[12] on the constants of the BeD and BeD^+ spectra would seem to favor Kronig's interpretation of such discrepancies.

In making accurate comparisons of the B_e constants one should of course consider the correction to B_e given by Dunham[13] in his extended treatment of the rotating vibrator. Calculation of the Dunham constants for AgH shows that this correction is of the order of one part in 75,000. The evaluation of the corresponding Dunham constants for AgD requires the analysis of at least one additional band, but approximate values may be obtained by application of regular isotope relations. This approximate solution gives a correction to B_e of the order of one part in 100,000. These corrections are too small to be of importance in the comparison of these spectra.

The author wishes to thank Professor W. W. Watson, who suggested the problem, for many helpful discussions during its progress.

---

[12] Koontz, Phys. Rev. **47**, 641 (1935).

[13] Dunham, Phys. Rev. **41**, 721 (1932).

JULY 15, 1935 PHYSICAL REVIEW VOLUME 48

The Theory of $^3\Sigma^+-{}^3\Sigma^-$ Transitions in Band Spectra[1]

RICHARD D. PRESENT, *Research Laboratory of Physics, Harvard University*

(Received May 20, 1935)

G. Herzberg has recently studied certain faint absorption bands in O_2 which show Q branches ($\Delta K=0$) but not the customary P and R branches ($\Delta K=\pm 1$). These bands he attributes on the basis of the configuration theory to a "forbidden" transition $^3\Sigma_g^- - {}^3\Sigma_u^+$. There exist two alternative explanations for the occurrence of these bands: (1) spin-orbit interaction, (2) rotational distortion. For the case of spin-orbit interaction the intensities have been calculated in case (a) and transformed to case (b) where the theory predicts twelve branches with $\Delta K=\pm 2,0$, provided that the J structure is resolved. When this structure is unresolved it is found that transitions with $\Delta K=0$ should be more intense than transitions with $\Delta K=\pm 2$ in the ratios: 6 : 1 for $K\doteq\infty$, 5 : 1 for $K=4$ and 4 : 1 for $K=1$. In view of the faintness of the observed bands this appears to be sufficient to account for the absence of branches with $\Delta K=0$. With rotational distortion, calculations show that only Q branches will occur. The intensities with spin-orbit interaction vary asymptotically as the first power of K, while for rotational distortion they increase asymptotically as K^3. Further experiments are needed to decide between the two explanations, although theory would favor the first from considerations of relative intensity. An explanation is given of the nonenhancement of the $^3\Sigma_g^- - {}^3\Sigma_u^+$ bands in O_4, despite the proximity of the triple-headed ultraviolet bands of Wulf, Finkelnburg and Steiner which we attribute to a $^3\Pi_g$ upper state. Transitions of the type $^1\Sigma^+ - {}^1\Sigma^-$ are also discussed.

INTRODUCTION

SEVERAL years ago Herzberg[2] discovered an unusual system of faint absorption bands in O_2 which appear between 2600 and 2400A and consist of but one branch apiece under the available dispersion of the quartz spectrograph. It appears conclusively from the experimental data that these bands have Q branches ($\Delta K=0$) but not the customary P and R branches ($\Delta K=\pm 1$)[3] and that they correspond to a "forbidden" transition between the ground state $^3\Sigma_g^-$ and an upper state $^3\Sigma_u^+$.[4]

---

[1] Presented at the Washington meeting of the American Physical Society, April, 1935.

[2] G. Herzberg, Naturwiss. **20**, 577 (1932).

[3] This is apparently the first time that such bands have been observed. In accordance with the positive-negative selection rule the only states which can combine with $^3\Sigma_g^-$ to give Q branches but no P or R branches are the states $^3\Sigma_u^+$ and $^1\Sigma_u^+$, of which only the former is a configuration arising from normal O atoms in a ^3P state. Since it can be shown from the experimental data that the upper state must dissociate into normal atoms, this leads to the interpretation of these bands as $^3\Sigma_g^- - {}^3\Sigma_u^+$.

[4] There is the possibility that these bands may be due to magnetic dipole radiation. The selection rules for this type of radiation require that positive levels should combine only with positive levels and negative only with negative (since the magnetic moment is invariant to reflection) and in consequence even (g) states will combine only with even states and odd (u) with odd. Then the only states which can combine with $^3\Sigma_g^-$ in the desired way are $^3\Sigma_g^-$ and $^1\Sigma_g^-$, of which the former alone is a configuration arising from normal atoms. Since but one $^3\Sigma_g^-$ state, *viz.*, the ground level, can arise in this way, we may conclude that magnetic dipole radiation is not responsible for the appearance of these bands.