

THE EMISSION SPECTRUM OF IBr EXCITED IN THE PRESENCE OF ARGON

Part II. The Band System in the Region 3915-3540 Å

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ABSTRACT

Wavelengths and wavenumbers of the band heads in the region 3915-3540 Å are recorded as obtained from the measurements of the plates taken on a first order 21-foot grating spectrograph. Earlier workers recently reported 40 bands of this system covering the region 3900-3800 Å. All the bands of this system obtained in the present experiments are analysed as involving the $^3\Pi(1)$ state for lower state. The constants for the lower state are such that they represent well the $\Delta G(v + \frac{1}{2})$ values obtained in the present experiments from $v = 0$ to $v = 26$ as well as those obtained by Brown from $v = 9$ to $v = 43$. The vibrational constants of the two states involved are:

$$\begin{array}{cccc} \omega_e'' & \omega_e'' x_e'' & \omega_e'' y_e'' & \omega_e z_e'' \\ 137.8 \text{ cm.}^{-1}, & 0.571 \text{ cm.}^{-1}, & -0.1156 \text{ cm.}^{-1} & 3.09 \times 10^{-3} \text{ cm.}^{-1} \\ \\ \omega_e'' t_e'' & \omega_e' & \omega_e' x_e' & \\ -2.5 \times 10^{-5} \text{ cm.}^{-1}, & 90.1 \text{ cm.}^{-1}, & 0.15 \text{ cm.}^{-1} & \end{array}$$

The probable electronic configurations and electronic terms for the different observed states of IBr are discussed.

INTRODUCTION

It was mentioned in the earlier paper¹ that IBr when excited in the presence of argon gives four band systems in the regions: (1) 5425-5360 Å, (2) 4520-4415 Å, (3) 4120-4010 Å and (4) 3915-3540 Å. Of these the first three were analysed and discussed in that paper and the last one will be analysed and discussed in this paper.

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EXPERIMENTAL RESULTS AND VIBRATIONAL ANALYSIS

The band system in the region 3915–3540 Å has been photographed with a 3-prism Steinheil glass spectrograph, a Hilger E₁ Littrow quartz spectrograph and a 21-foot grating spectrograph in the first order. Figures 1 and 2 show the system 3915–3540 Å as obtained with these different spectrographs. The wavelengths and wavenumbers of the band heads measured from the plates taken on the 21-foot grating spectrograph are given in Table I in which

TABLE I
*Wavelengths, wavenumbers and intensities of the bands in the
3915–3540 Å system*

| I | λ_{air} | ν_{vac} | I | λ_{air} | ν_{vac} |
|---|------------------------|--------------------|----|------------------------|--------------------|
| 0 | 3915.7 | 25531 | 1 | 3884.8 | 25734* |
| 1 | 3914.0 | 25542* | 1 | 3884.1 | 25739 |
| 1 | 3913.0 | 25549 | 4 | 3883.3 | 25744 |
| 1 | 3910.6 | 25564 | 3 | 3882.3 | 25751* |
| 2 | 3908.3 | 25579 | 3 | 3881.4 | 25757 |
| 1 | 3906.2 | 25593 | 3 | 3877.9 | 25780 |
| 0 | 3904.5 | 25604* | 5 | 3877.3 | 25784 |
| 0 | 3903.7 | 25609 | 10 | 3876.5 | 25789 |
| 2 | 3902.7 | 25616 | 4 | 3872.7 | 25814 |
| 3 | 3901.9 | 25621 | 5 | 3871.5 | 25822 |
| 2 | 3901.1 | 25627 | 5 | 3869.6 | 25835 |
| 1 | 3899.4 | 25638 | 5 | 3868.1 | 25844 |
| 1 | 3898.1 | 25646 | 10 | 3865.2 | 25864 |
| 2 | 3895.4 | 25664 | 3 | 3864.3 | 25871 |
| 5 | 3893.6 | 25676 | 3 | 3863.4 | 25877 |
| 4 | 3892.6 | 25683 | 2 | 3861.5 | 25889 |
| 2 | 3890.5 | 25696 | 10 | 3860.4 | 25897 |
| 1 | 3890.0 | 25700 | 3 | 3859.8 | 25901 |
| 4 | 3888.7 | 25708 | 5 | 3858.8 | 25907 |
| 2 | 3887.6 | 25716 | 2 | 3857.9 | 25914 |
| 2 | 3885.5 | 25729 | 2 | 3857.3 | 25918 |

TABLE I (Contd.)

| I | λ_{air} | ν_{vac} | I | λ_{air} | ν_{vac} |
|---|------------------------|--------------------|---|------------------------|--------------------|
| 0 | 3855.1 | 25932 | 1 | 3823.4 | 26147 |
| 9 | 3854.4 | 25937 | 5 | 3822.9 | 26151 |
| 4 | 3853.7 | 25941 | 5 | 3822.5 | 26153 |
| 4 | 3852.6 | 25949 | 1 | 3820.5 | 26167 |
| 5 | 3850.7 | 25962 | 2 | 3819.5 | 26174 |
| 3 | 3849.9 | 25967 | 3 | 3818.2 | 26183 |
| 3 | 3849.4 | 25971 | 2 | 3816.3 | 26196 |
| 3 | 3848.9 | 25974 | 2 | 3815.0 | 26205 |
| 3 | 3847.8 | 25982 | 2 | 3813.5 | 26215 |
| 4 | 3845.5 | 25997 | 3 | 3812.1 | 26225 |
| 0 | 3843.9 | 26008 | 3 | 3808.8 | 26248 |
| 2 | 3842.7 | 26016 | 2 | 3807.5 | 26257 |
| 8 | 3840.9 | 26028 | 2 | 3806.4 | 26264 |
| 8 | 3839.9 | 26035 | 3 | 3805.4 | 26271 |
| 2 | 3839.2 | 26040 | 0 | 3804.2 | 26279* |
| 1 | 3838.5 | 26044 | 1 | 3803.5 | 26284* |
| 3 | 3837.7 | 26050 | 4 | 3802.7 | 26290 |
| 3 | 3837.3 | 26053 | 4 | 3800.7 | 26304 |
| 3 | 3836.9 | 26055 | 4 | 3797.3 | 26327 |
| 7 | 3834.5 | 26072 | 2 | 3796.4 | 26333 |
| 2 | 3833.5 | 26079 | 2 | 3795.2 | 26342 |
| 3 | 3833.0 | 26082 | 3 | 3792.3 | 26362 |
| 3 | 3831.6 | 26091 | 3 | 3791.9 | 26364 |
| 1 | 3830.4 | 26100 | 3 | 3789.8 | 26379 |
| 4 | 3829.4 | 26107 | 3 | 3789.3 | 26382 |
| 3 | 3826.9 | 26123 | 2 | 3786.7 | 26401 |
| 3 | 3826.0 | 26130 | 2 | 3786.3 | 26404 |
| 5 | 3824.6 | 26139 | 3 | 3784.4 | 26417 |
| 5 | 3824.2 | 26142 | 3 | 3784.0 | 26420 |

TABLE I (Contd.)

| I | λ_{air} | λ_{vac} | I | λ_{air} | λ_{vac} |
|---|------------------------|------------------------|---|------------------------|------------------------|
| 2 | 3782.5 | 26430 | 2 | 3752.8 | 26639 |
| 1 | 3781.3 | 26438 | 3 | 3751.9 | 26646 |
| 3 | 3779.9 | 26448 | 3 | 3751.6 | 26648 |
| 3 | 3779.5 | 26451 | 1 | 3751.2 | 26651 |
| 3 | 3778.8 | 26456* | 1 | 3749.9 | 26660 |
| 3 | 3778.4 | 26459 | 1 | 3749.0 | 26666 |
| 2 | 3777.2 | 26467 | 1 | 3748.1 | 26673 |
| 2 | 3776.3 | 26473 | 2 | 3747.2 | 26679 |
| 2 | 3775.5 | 26479 | 3 | 3746.6 | 26683 |
| 1 | 3775.1 | 26482 | 4 | 3745.5 | 26691 |
| 1 | 3773.9 | 26490 | 2 | 3742.5 | 26713 |
| 3 | 3772.4 | 26501 | 1 | 3741.5 | 26720 |
| 3 | 3772.1 | 26503 | 0 | 3739.4 | 26735 |
| 2 | 3770.2 | 26516 | 0 | 3738.3 | 26743 |
| 2 | 3769.4 | 26529 | 1 | 3737.4 | 26749* |
| ? | 3768.0 | 26532 | 0 | 3735.9 | 26760 |
| 1 | 3767.1 | 26538 | 1 | 3733.2 | 26779* |
| 1 | 3765.3 | 26551* | 1 | 3732.7 | 26783 |
| 2 | 3764.9 | 26554 | 1 | 3732.0 | 26788 |
| 4 | 3763.3 | 26565 | 1 | 3731.3 | 26793 |
| 4 | 3761.8 | 26575 | 1 | 3730.7 | 26797* |
| 2 | 3760.2 | 26588 | 1 | 3728.1 | 26818 |
| 2 | 3758.3 | 26600 | 1 | 3727.3 | 26821 |
| 1 | 3757.6 | 26605 | 0 | 3726.5 | 26827 |
| 2 | 3757.2 | 26608 | 1 | 3723.6 | 26848 |
| 2 | 3756.7 | 26612* | 2 | 3722.2 | 26858 |
| 2 | 3755.3 | 26621 | 2 | 3721.5 | 26864* |
| 1 | 3754.9 | 26624* | 1 | 3720.6 | 26870 |
| 0 | 3754.3 | 26629* | 0 | 3720.2 | 26873 |

TABLE I (Contd.)

| I | λ_{air} | λ_{vac} | I | λ_{air} | λ_{vac} |
|---|------------------------|------------------------|---|------------------------|------------------------|
| 1 | 3719.6 | 26877 | 2 | 3683.6 | 27140 |
| 0 | 3718.7 | 26883 | 0 | 3682.4 | 27148 |
| 2 | 3717.2 | 26894 | 2 | 3680.1 | 27166 |
| 2 | 3716.8 | 26897 | 2 | 3678.9 | 27174 |
| 1 | 3714.9 | 26911 | 0 | 3676.5 | 27192 |
| 1 | 3713.8 | 26919 | 1 | 3675.4 | 27200* |
| 1 | 3711.7 | 26934 | 0 | 3672.9 | 27219 |
| 0 | 3711.1 | 26939 | 0 | 3672.0 | 27225 |
| 2 | 3709.8 | 26948* | 0 | 3671.5 | 27229 |
| 2 | 3709.0 | 26954 | ? | 3670.6 | 27236 |
| 1 | 3708.1 | 26960 | ? | 3670.0 | 27240 |
| 0 | 3707.2 | 26967 | 1 | 3669.2 | 27246 |
| 2 | 3704.5 | 26987 | 2 | 3668.2 | 27254 |
| 1 | 3702.3 | 27003 | 2 | 3667.9 | 27256* |
| 1 | 3701.7 | 27007 | 2 | 3666.9 | 27263 |
| 1 | 3699.9 | 27020 | 1 | 3665.9 | 27271 |
| 1 | 3698.5 | 27030* | 2 | 3664.3 | 27283* |
| 1 | 3697.8 | 27035 | 2 | 3663.3 | 27290* |
| 0 | 3696.3 | 27046 | 2 | 3662.3 | 27298 |
| 1 | 3695.3 | 27054 | 1 | 3661.5 | 27304 |
| 1 | 3694.4 | 27060* | 0 | 3660.7 | 27310 |
| 2 | 3692.7 | 27073 | 1 | 3659.6 | 27318 |
| 2 | 3690.2 | 27091 | 2 | 3658.7 | 27324 |
| 1 | 3689.3 | 27098 | 2 | 3657.9 | 27331 |
| 0 | 3688.4 | 27104 | 1 | 3656.8 | 27338 |
| 1 | 3686.4 | 27119* | 1 | 3655.8 | 27346 |
| 1 | 3686.0 | 27122* | 0 | 3655.3 | 27350 |
| 1 | 3685.5 | 27125* | 2 | 3654.6 | 27355 |
| 1 | 3684.6 | 27133 | 2 | 3653.5 | 27363 |

TABLE I (Contd.)

| I | λ_{air} | ν_{vac} | I | λ_{air} | ν_{vac} |
|---|------------------------|--------------------|---|------------------------|--------------------|
| 2 | 3652.1 | 27374 | 1 | 3622.4 | 27598* |
| 2 | 3651.2 | 27380 | 0 | 3621.3 | 27607 |
| ? | 3650.5 | 27386 | 1 | 3620.3 | 27614* |
| 0 | 3649.5 | 27393 | ? | 3619.5 | 27621 |
| 2 | 3645.3 | 27410 | 1 | 3618.1 | 26631 |
| 2 | 3646.8 | 27413 | 1 | 3617.6 | 27635* |
| 1 | 3644.8 | 27429 | 0 | 3617.2 | 27638 |
| 1 | 3643.8 | 27437 | 0 | 3616.9 | 27640* |
| 0 | 3642.8 | 27444 | 1 | 3615.9 | 27648 |
| 0 | 3640.2 | 27463 | 2 | 3615.6 | 27650 |
| 1 | 3639.3 | 27470 | 2 | 3614.5 | 27658 |
| 1 | 3639.0 | 27472 | 1 | 3613.4 | 27667 |
| 0 | 3638.2 | 27478 | 1 | 3613.0 | 27670* |
| 1 | 3634.7 | 27504 | 1 | 3612.5 | 27674* |
| 1 | 3634.2 | 27509* | 1 | 3610.8 | 27687 |
| 2 | 3632.1 | 27524 | 0 | 3610.2 | 27691 |
| 2 | 3631.6 | 27528 | 1 | 3609.0 | 27701 |
| 1 | 3629.0 | 27548 | 1 | 3605.3 | 27729 |
| ? | 3627.9 | 27556 | 1 | 3600.0 | 27770 |
| 1 | 3627.5 | 27560 | 1 | 3599.6 | 27773 |
| 1 | 3626.1 | 27570 | 1 | 3593.9 | 27817 |
| 1 | 3625.6 | 27574 | 2 | 3585.6 | 27882 |
| 1 | 3625.1 | 27578* | 1 | 3570.6 | 27999 |
| 2 | 3624.0 | 27586 | 1 | 3555.6 | 28117 |
| 0 | 3623.7 | 27589* | 1 | 3541.5 | 28229 |

Note.—Bands marked (*) in the above table are not put in the vibrational scheme shown in Table II. Some of these bands can be accounted as isotopic bands and some can be put in Table II with error more than what is allowed for the bands put in that table.

the visually estimated relative intensities are also included. The error involved may be estimated to be about $\pm 2 \text{ cm.}^{-1}$. This band system is the most exten-

sive of all the different band systems of IBr obtained in the present experiments. Haranath and Rao,² exciting IBr with a condensed transformer discharge, reported recently about 40 bands in the region 3900–3800 Å. They analysed the bands obtained by them as due to transition from an upper level at 38306 cm.⁻¹ with $\omega_e = 104$ cm.⁻¹ and $\omega_e x_e = 0.8$ cm. to the ${}^3\Pi(1)$ state at $T_e = 12230$ cm.⁻¹ reported earlier by Brown³ from the near infrared absorption band system. It was not possible to represent all the bands obtained in the present experiments with the above constants obtained by Haranath and Rao.* In fact even the 40 bands obtained by them are not well represented with these constants, as all the $\Delta G(v + \frac{1}{2})$ values observed according to their analysis are all higher than those calculated according to the constants they used. However, their view that the lower state involved for the system is the ${}^3\Pi(1)$ state is supported by the vibrational analysis given in this paper.

The Deslandres scheme of the band system representing all the bands is given in Table II and the corresponding intensity distribution in Table III.

The $\Delta G(v + \frac{1}{2})$ values obtained from Table II are listed in Table IV along with the $\Delta G(v + \frac{1}{2})$ values obtained by Brown³ for the upper state ${}^3\Pi(1)$ of the near infrared absorption system of IBr. The two sets of the $\Delta G(v + \frac{1}{2})$ values are plotted against v in Fig. 3 and all the points could be represented well by a smooth curve. This suggests that both the sets of $\Delta G(v + \frac{1}{2})$ values represent the same electronic state. It was found that all the $\Delta G(v + \frac{1}{2})$ values can satisfactorily be represented with the constants $\omega_0 = 137.05$ cm.⁻¹, $\omega_0 x_0 = 0.74$ cm.⁻¹, $\omega_0 y_0 = 0.1095$ cm.⁻¹, $\omega_0 z_0 = 3.03 \times 10^{-3}$ cm.⁻¹ and $\omega_0' = 2.5 \times 10^{-5}$ cm.⁻¹. The calculated $\Delta G(v + \frac{1}{2})$ values are also included in Table IV and plotted in Fig. 3. All the bands in Table I were thus found to be fairly well represented with the formula†

* Further because of the higher anharmonicity factor the dissociation energy of the upper state by linear extrapolation comes to only 3328 cm.⁻¹, giving 41431 cm.⁻¹ for the energy of dissociation products, whereas the nearest expected level of dissociation products are too far off from this. This would mean that the actual dissociation energy will be so many times higher than the D_0 obtained. Therefore it is necessary either to decrease the anharmonicity considerably if possible or to add up positive higher order terms so that the dissociation energy could be increased considerably. It may be also noted that the ν_0 value of 26076 cm.⁻¹ given by them for this system is wrongly calculated, as it should be 25954.5 cm.⁻¹ according to their analysis.

† The linear extrapolation using the ω_0' and $\omega_0' x_0'$ of this formula gives $D_0' = 13500$ cm.⁻¹ which leads to the value of 52124 cm.⁻¹ for the energy of the dissociation products compared to the value of 41431 cm.⁻¹ that one gets from the constants used by Haranath and Rao.² This value of 52124 cm.⁻¹ is still lower than the nearest expected level of dissociation products. The actual D_0' is therefore larger than that one obtains by linear extrapolation and this is an indication that the state involved is probably an ionic state.^{6,7} It is likely that certain positive higher order terms like $\omega_0' y_0' v'^3$ are involved which become appreciable at larger v' values than those observed and lead to a higher value for D_0' than that one obtains by linear extrapolation.

$$\nu = 26476 + (90.0 v' - 0.15 v'^2) - (137.5 v'' - 0.74 v''^2 - 0.1095 v''^3 + 3.03 \times 10^{-3} v''^4 - 2.5 \times 10^{-5} v''^5)$$

TABLE III

Intensity distribution and Frank-Condon parabola of the band system 3915–3540 Å

| $v'' \backslash v'$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 |
|---------------------|---|---|---|---|---|---|----|----|---|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 0 | 2 | 2 | 2 | 7 | 4 | 5 | 1 | 2 | | | | | | | | | | | | | | | | | | | | |
| 1 | 4 | 2 | 4 | 1 | 8 | 2 | 10 | 5 | 1 | | | | | | | | | | | | | | | | | | | |
| 2 | 3 | 2 | 3 | 2 | 3 | | 3 | | | | | | | | | | | | | | | | | | | | | |
| 3 | 0 | 2 | 2 | 2 | 2 | 3 | 3 | 10 | 4 | 1 | 0 | | | | | | | | | | | | | | | | | |
| 4 | | 4 | 2 | 4 | 3 | 3 | 4 | 5 | 2 | 2 | | | | | | | | | | | | | | | | | | |
| 5 | 1 | 1 | 3 | 2 | | 3 | 1 | 8 | 2 | 4 | 4 | 2 | | | | | | | | | | | | | | | | |
| 6 | 1 | 0 | 0 | 2 | 1 | 3 | | 3 | 0 | 3 | | 1 | 0 | | | | | | | | | | | | | | | |
| 7 | 1 | 1 | 0 | | | 3 | 4 | 2 | 1 | | 2 | 10 | 2 | 0 | | | | | | | | | | | | | | |
| 8 | | 0 | 1 | 1 | 1 | 7 | 3 | | 3 | 2 | 3 | 3 | 5 | 2 | | | | | | | | | | | | | | |
| 9 | 1 | 7 | 1 | 1 | 0 | 2 | 3 | 3 | 3 | | | 3 | 3 | 3 | 1 | 3 | | | | | | | | | | | | |
| 10 | 2 | 0 | 2 | 1 | 0 | | 2 | 2 | 3 | 2 | 5 | 3 | 5 | 10 | 10 | 4 | 1 | | | | | | | | | | | |
| 11 | 0 | 0 | 2 | 0 | 1 | 1 | 2 | | 3 | | | 5 | 1 | | 3 | | | | | | | | | | | | | |
| 12 | | 0 | 2 | 1 | 1 | 0 | 0 | 3 | 0 | | 4 | 3 | 3 | 2 | 5 | | | 1 | 5 | | | | | | | | | |
| 13 | 7 | 0 | 0 | 0 | 2 | 0 | 1 | | 2 | 0 | | | 2 | 3 | 1 | 3 | 10 | 5 | 3 | 1 | 1 | 1 | | | | | | |
| 14 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | | 2 | | | 4 | 2 | 3 | 3 | 3 | 2 | 5 | 10 | 2 | 4 | | | | | | |
| 15 | | 2 | 2 | 0 | 2 | 2 | 1 | | | 3 | | | 4 | 2 | 5 | | 4 | 0 | 3 | 4 | | 2 | | | | | | |
| 16 | | | 0 | 1 | 0 | 0 | 0 | 2 | 1 | | 1 | | | 4 | 3 | 5 | 3 | 2 | 5 | 5 | | | | | | | | |
| 17 | | | | 1 | 1 | 0 | 0 | 2 | 1 | | | | | | | | | 1 | 4 | 1 | | 9 | 2 | 5 | | | | |
| 18 | | | | 1 | 2 | 0 | 1 | | 0 | 0 | | | | | | | | 3 | 3 | 7 | | 3 | 0 | | | | | |
| 19 | 1 | | 1 | 0 | 0 | 2 | ? | | 1 | 1 | 1 | | | | | | 2 | 2 | 3 | 2 | 5 | 4 | 3 | 2 | | | | |
| 20 | | | 1 | 1 | 1 | 0 | 2 | | | | | | 1 | | | | 3 | | | | | 5 | 1 | | | | | |
| 21 | | | | 1 | 1 | 2 | 2 | 2 | | | | | | | 3 | | | 1 | 3 | 4 | 3 | 3 | 3 | 1 | 4 | | | |
| 22 | | | | | 1 | 0 | | 2 | 1 | 2 | | | 2 | | | | | | 2 | 2 | | | 2 | 3 | 2 | | | |
| 23 | | | | | 1 | 0 | 1 | 1 | 2 | 2 | | | | 2 | | | 1 | | | 1 | 1 | | | | 3 | | | |
| 24 | | | | | | 1 | 2 | 1 | 1 | 1 | 1 | 0 | 1 | 2 | | | 4 | | | 3 | 2 | 2 | | | | | | 4 |
| 25 | | | | | | | | 1 | 2 | | 2 | ? | 2 | 1 | | | | 2 | | 1 | 2 | 2 | 2 | 1 | 2 | 3 | | |
| 26 | | | | | | | | | | 0 | 1 | 0 | 0 | 2 | | | | 2 | | | | | | | 2 | 2 | 1 | 3 |
| 27 | | | | | | | | | | 1 | 2 | 0 | 1 | 0 | | | | | | | | | | | | 1 | 0 | 1 |
| 28 | | | | | | | | | 2 | | 1 | 1 | 0 | ? | 1 | | | | 2 | | | | | | | | | 2 |
| 29 | | | | | | | | | | | | 2 | ? | 1 | ? | | | | | 1 | | | | | | | | |
| 30 | | | | | | | | | | | | | 0 | | | | | | | | | | | | | | | |
| 31 | | | | | | | | | 1 | 1 | | | | | | | | | | | | | | | | | | |

TABLE IV

The $\Delta G(v + \frac{1}{2})$ values for the ${}^3\Pi(1)$ state of IBr at $T_0 = 12148 \text{ cm.}^{-1}$

| v | Observed $\Delta G(v + \frac{1}{2})$ cm. ⁻¹ | Brown $\Delta G(v + \frac{1}{2})$ cm. ⁻¹ | Calculated $\Delta G(v + \frac{1}{2})$ cm. ⁻¹ |
|-----|--|---|--|
| 0 | 135.4 | .. | 136.2 |
| 1 | 134.5 | .. | 134.1 |
| 2 | 129.7 | .. | 131.5 |
| 3 | 127.6 | .. | 128.3 |
| 4 | 123.0 | .. | 124.8 |
| 5 | 121.3 | .. | 120.9 |
| 6 | 116.3 | .. | 116.6 |
| 7 | 111.5 | .. | 112.2 |
| 8 | 107.0 | .. | 107.5 |
| 9 | 103.3 | 103 | 102.7 |
| 10 | 98.1 | 96 | 97.8 |
| 11 | 92.3 | 94 | 92.8 |
| 12 | 89.3 | 88 | 87.9 |
| 13 | 83.2 | 86 | 82.9 |
| 14 | 79.3 | 79 | 78.0 |
| 15 | 71.0 | 73 | 73.1 |
| 16 | 70.5 | 68 | 68.4 |
| 17 | 64.3 | 65 | 63.8 |
| 18 | 57.7 | 59 | 59.3 |
| 19 | 58.0 | 54 | 55.1 |
| 20 | 51.5 | 51 | 51.0 |
| 21 | 48.8 | 46 | 47.1 |
| 22 | 42.3 | 43 | 43.5 |
| 23 | 40.7 | 40 | 40.0 |
| 24 | 35.5 | 34 | 36.8 |
| 25 | 32.0 | 36 | 33.8 |
| 26 | 31.0 | 29 | 31.0 |
| 27 | .. | 30 | 28.5 |
| 28 | .. | 25 | 26.1 |
| 29 | .. | 23 | 24.0 |
| 30 | .. | 22 | 22.0 |
| 31 | .. | 21 | 20.2 |
| 32 | .. | 19 | 18.5 |
| 33 | .. | 19 | 17.0 |
| 34 | .. | 16 | 15.5 |
| 35 | .. | 14 | 14.2 |
| 36 | .. | 12 | 12.8 |
| 37 | .. | 10 | 11.5 |
| 38 | .. | 9 | 10.1 |
| 39 | .. | 9 | 8.6 |
| 40 | .. | 8 | 7.0 |
| 41 | .. | 5 | 5.2 |
| 42 | .. | 4 | 3.2 |
| 43 | .. | 4 | 1.0 |

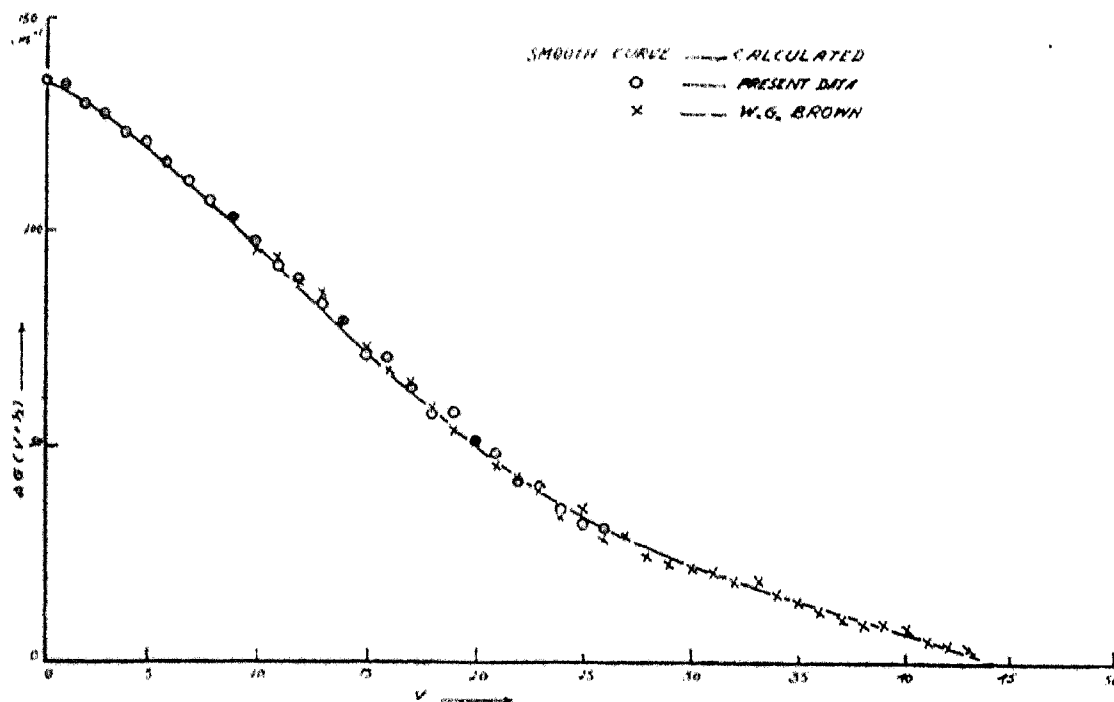


Fig. 3. The graph showing the $\Delta G(v + \frac{1}{2})$ versus v of ${}^2II(1)$ state of IBr at $T_e = 12213 \text{ cm.}^{-1}$. The deviation between the observed and calculated values of the band heads is mostly within $\pm 3 \text{ cm.}^{-1}$ and for some cases $\pm 4 \text{ cm.}^{-1}$. Only in very few cases it is $\pm 5 \text{ cm.}^{-1}$.

As Brown did not observe any bands with $v' \geq 9$ in the near infrared absorption band system, he had to use a long extrapolation to obtain v_e and ω_e of the upper state of the absorption band system. The $\Delta G(v + \frac{1}{2})$ values for this level are known from the present experiments up to $v = 0$ and therefore it is not necessary to use such a long extrapolation. Using the vibrational constants obtained above for this state along with the absorption data of Brown, the T_0 and T_e for this level are obtained to be 12148 cm.^{-1} and 12213 cm.^{-1} respectively. The position of the upper level of the system thus comes out to be $T_0 = 38624 \text{ cm.}^{-1}$ or $T_e = 38714 \text{ cm.}^{-1}$.

ISOTOPIC SHIFT

As bromine has two equally abundant stable isotopes Br^{79} and Br^{81} , each vibrational band of the IBr system is expected to be doublet. But the bands in the system $3915\text{--}3540 \text{ \AA}$ lie very much close together and overlap one another, so that it is difficult to identify any isotopic shift unambiguously.

ELECTRONIC TRANSITIONS INVOLVED

The positions of all the stable states of IBr molecule including those observed by the earlier workers are given along with the vibrational constants in Table V. The band systems to which the different levels are responsible

TABLE V
Observed States of Iodine Bromide Molecule*

| Electronic Configuration in terms of molecular orbitals No. of/ | | Electron States | | Name ^d | Position of the levels ^b cm. ⁻¹ | | ω_e cm. ⁻¹ | ω_e cm. ⁻¹ | Dissociation ^e products ^f | Remarks |
|---|-------|------------------------|---------------------------------|-------------------|--|----------------|------------------------------|------------------------------|---|--|
| σ | π | Case a or b type | Case c or Ω_s type | | T ₀ | T _e | | | | |
| .. | .. | .. | .. | I | $a_0 + 24524$ | $a_e + 24540$ | 128.3 | 128.4 | ex | I → H gives emission bands in the region 4120-4010 Å in the presence of argon (Ref. 1) |
| .. | .. | .. | .. | H | a_0 | a_e | 159.5 | 160.6 | ex | .. |
| 2 | 4 | .. | $II_{1,0+}$ | G | 56369 | .. | (310) | .. | ex | X → G gives absorption bands in the vacuum ultraviolet region (Cordes and Spomer ⁵) |
| 2 | 4 | σ^x | II_1 | F | 51701 | .. | (314) | .. | ex | X → F gives absorption bands in the vacuum ultraviolet region (Ref. 5) |
| 2 | 3 | $^1\Sigma^+$ | 0+ | E | 39030 | 39126 | 76.5 | 77.0 | ex | E → B' gives emission band system in the region 4520-4415 Å in the presence of argon (Ref. 1) |
| 2 | 3 | $^1\Delta$ | 2 | D | 38623 | 38713 | 90.0 | 90.1 | ex | D → A gives emission band system in the region 3915-3540 Å in the presence of argon (discussed in the present paper) |
| 2 | 3 | $^3\Sigma^-$ | 1 or 0+ | C | 35314 | 35427 | 43.0 | 43.03 | ex | C → B' gives emission band system in the region 5425-5360 Å in the presence of argon (Ref. 1) |
| 2 | 3 | 3II | 0+ | B' | 16712 | 16814 | 65.3 | 65.5 | bb | X → B' gives absorption bands in the region 6186-5458 Å (Brown ³) |
| 2 | 4 | 3II | 0+ | B | 16112 | 16155 | (145.7) | (150) | ab | X → B gives absorption bands in the region 6764-6240 Å (Brown ³) |
| 2 | 4 | 3II | 1 | A | 12148 | 12213 | 137.1 | 137.8 | aa | X → A gives absorption bands in the region 8000-817 Å (Brown ³) |
| 2 | 4 | $^1\Sigma^+$ | 0+ | X | 0 | 0 | 267.6 | 268.4 | aa | Ground State |

* The term scheme is mainly based upon that given by Mulliken⁴ for ICl.

^b Under dissociation products aa mean $I^2P_{3/2} + Br^2P_{3/2}$ atoms, ab means $I^2P_{3/2}$ atoms, bb means $I^2P_{3/2} + Br^2P_{3/2}$ atoms and ex means either iodine and bromine atoms or iodine and bromine atoms of which one, at least, is excited.

^c The names to the levels are given according to their heights. The designations for the levels at 56369 and 51701 cm.⁻¹ are now G and F instead of D and C used by Herzberg.

^d The values given in brackets () are only approximate.

^e In this column σ represents a bonding orbital of the form ($4p_{\sigma_{Br}} + 5p_{\sigma_{I}}$), π , π represent orbitals of the form ($4p_{\pi_{Br}} + 5p_{\pi_{I}}$), ($5p_{\pi_{I}}$ - $4p_{\pi_{Br}}$) if molecular orbital approximation is used for the π electrons. If atomic orbital approximation is used for the π electrons, π , π in the first column of the table stands for $4p_{\pi_{Br}}$ and $5p_{\pi_{I}}$ respectively. σ^x stands for ($5p_{\sigma_{I}}$ - $4p_{\sigma_{Br}}$) which is anti-bonding. σ^* stands for an orbital of the electron which has gone to $(z+1)s\sigma$ orbit from $np\pi$ orbit.

^f The levels named C, D and E may be having positive higher order vibrational constants (like ω_2, ω_3 , etc.) which becomes significant at higher vibrational levels than those observed and take the dissociation limits to higher proper positions than those one would get by linear extrapolation.

are given in the last column of the table. It is more difficult in the case of IBr than in the case of I_2 and Br_2 to determine the electronic configurations and the electronic terms for the different observed levels. This is because the absence of the *gerade* and *ungerade* classification of the terms increases the number of the allowed transitions. However, with the help of term scheme developed by Mulliken⁴ for ICl and taking analogies from I_2 and Br_2 molecules, it is possible to arrive at certain tentative conclusions about the electronic configurations and electronic terms of the states involved.

The electronic configurations and the electronic terms, responsible for the states X, A, B, B', F and G given in Table V, are those suggested by Mulliken.⁴ The new states that are observed in the present experiments are C, D, and E at 35314 cm.^{-1} , 38623 cm.^{-1} and 39030 cm.^{-1} respectively and H and I at undetermined positions ' a_0 ' and ' a_0 ' + 25244 cm.^{-1} respectively. Of these the states C and E form the upper levels of the systems $5425\text{--}5360\text{ \AA}$ and $4520\text{--}4415\text{ \AA}$ respectively discussed in the earlier paper.¹ The state D forms the upper level of the $3915\text{--}3540\text{ \AA}$ system discussed in this paper. All these states have very low vibrational frequencies and it is quite likely that the electronic configurations for these states will involve two anti-bonding σ electrons. The first two such electronic configurations according to Mulliken⁴ are $\sigma^2\pi^4\pi^3\sigma^*$ and $\sigma^2\pi^3\pi^3\sigma^{*2}$. Of these the $\sigma^2\pi^4\pi^3\sigma^*$ configuration gives the states $^1\Sigma^+(0^+)$, $^1\Delta(2)$ and $^3\Sigma^-(1, 0^+)$ which according to Mulliken's Table⁴ for ICl as well as on analogy with similar states of I_2 and Br_2 , are expected to dissociate into normal $^3P + ^3P$ atoms of iodine and bromine. It is, therefore, likely that the configuration $\sigma^2\pi^4\pi^3\sigma^*$ is responsible for the three states C, D and E. The configuration $\sigma^2\pi^3\pi^3\sigma^{*2}$ gives rise to the electronic terms $^1\Sigma^+(0^+)$, $^3\Delta(3, 2, 1)$, $^3\Sigma^-(1, 0^+)$, $^1\Sigma^+(0^+)$, $^1\Delta(2)$ and $^3\Sigma^-(0^+, 1)$ of which the first three are expected to dissociate into normal $^3P + ^3P$ iodine and bromine atoms and are, therefore, probably repulsive states whereas the last three are expected to dissociate into iodine and bromine ions or into iodine and bromine atoms of which one, at least, is in excited state and therefore, they are probably stable. The three electronic terms $^1\Sigma^+(0^+)$, $^1\Delta(2)$ and $^3\Sigma^-(0^+ \text{ or } 1)$ can, therefore, be tentatively assigned to the states E, D and C respectively. It may be noted that the ω_e values for the different states arising from the same configuration are expected to be nearer to one another, but the ω_e value for the C state is only 43.03 cm.^{-1} whereas the ω_e values for

‡ Incidentally it may be mentioned that Haranath and Rao³ appear to have overlooked the details given by Mulliken's Table⁴ and state wrongly that the states arising in the configuration $\sigma^2\pi^4\pi^3\sigma^*$ are predicted by Mulliken to dissociate into $I^+ + Cl^-$.

the D and E are 90.1 and 77.0 cm.^{-1} respectively. This may be because these states might be having different dissociation products.[§]

The assignment of electronic configurations for the H and I states will be more difficult than the assignment for the levels C, D and E, as even the exact positions of these levels are not yet determined. The electronic configurations for the states H and I are, therefore, not included in Table V.

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[§] The $^3\Pi_u(I_u)$ and $^3\Pi_u(O_u^+)$ states of iodine arising from the same configuration $\sigma_g^2\pi_u^4\sigma_g^2\sigma_u$ are known to have ω_e values 40 and 128 cm.^{-1} respectively which is understood on the basis that they have different dissociation products.

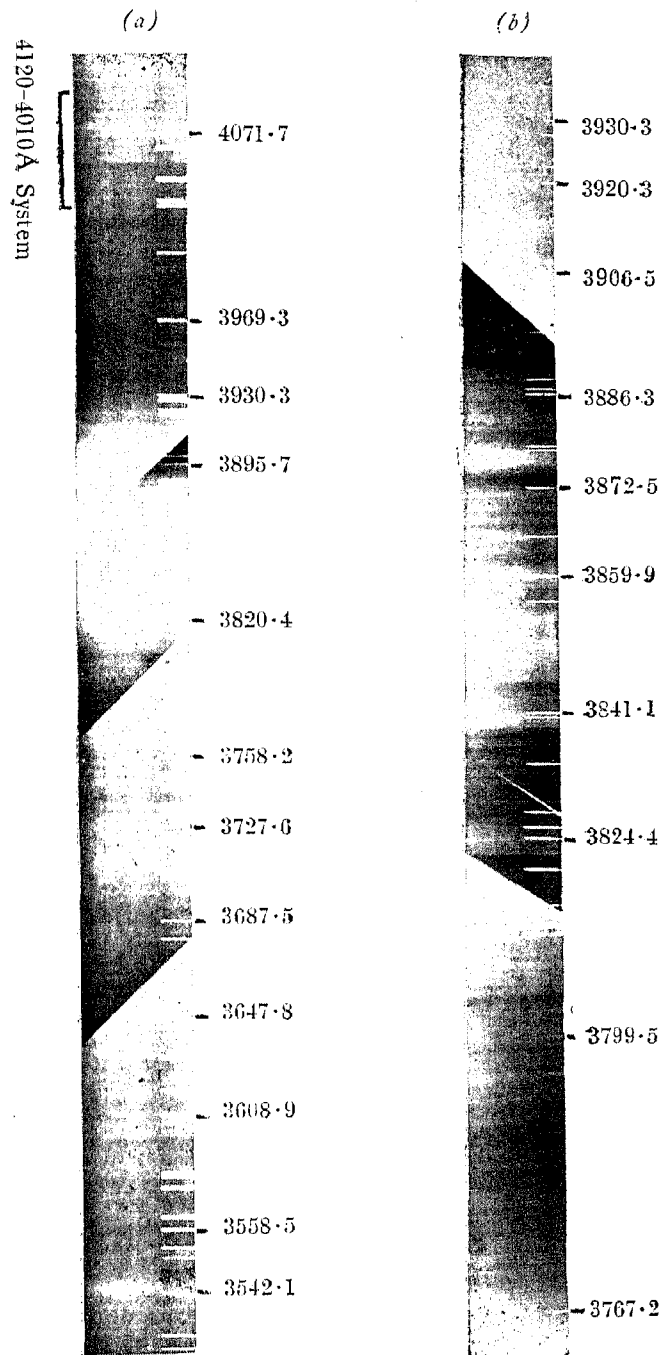


FIG. 1.

(a) Enlargement of the spectrum of IBr excited in the presence of argon taken with a Hilger E_1 Littrow quartz spectrograph in the region 4120–3540 Å. (b) Enlargement of the band system 3915–3540 Å of IBr taken with Steinheil 3-prism glass spectrograph in the region 3930–3760 Å.

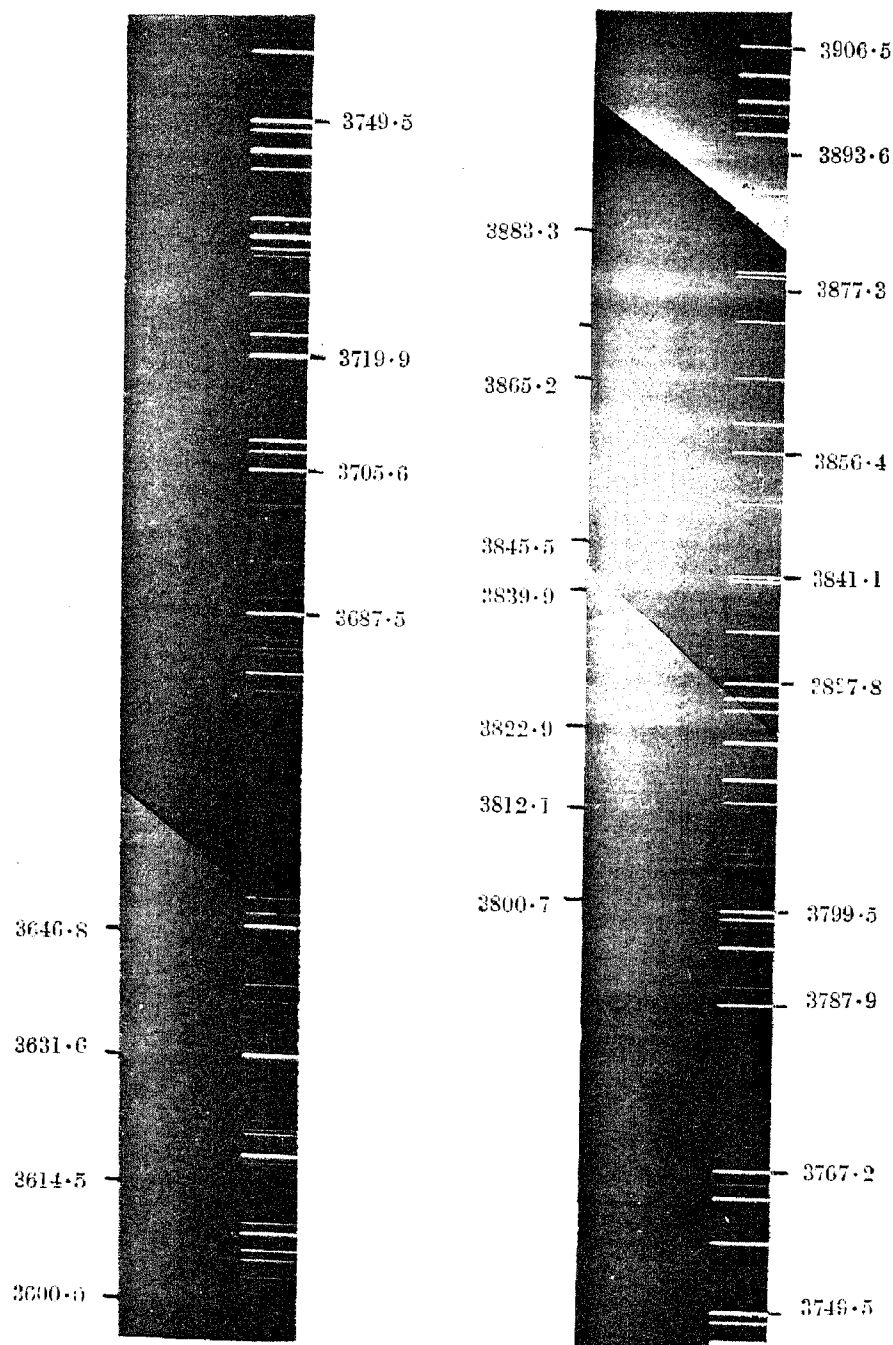


FIG. 2. Enlargement of 3915-3540 Å system of IBr taken with 21-foot grating spectrograph in the first order.