# RADIATIVE LIFETIME OF THE $B^{3} \Pi_{o^{+}}$STATE OF $\mathrm{Br}_{2}$ 

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#### Abstract

The absorption and fluorescence spectra of the molecule bromine corresponding to the transition between the ground state, $X^{1} \Sigma_{o^{+} g}$, and excited state, $B^{3} \Pi_{o^{+} u}$, have been measured from approximately $17464 \mathrm{~cm}^{-1}$ to $17480 \mathrm{~cm}^{-1}$. This region of the spectra covered the $14^{\prime}-1^{\prime \prime}, 15^{\prime}-1^{\prime \prime}, 17^{\prime}-2^{\prime \prime}, 18^{\prime}-2^{\prime \prime}$, and $19^{\prime}-2^{\prime \prime}$ vibrational bands. The frequency of each absorption line was calculated and the integrated absorption coefficient under each absorption line was measured. At room temperature, the number of molecules per $\mathrm{cm}^{3}$ for ${ }^{(79,79)} B r_{2},{ }^{(79,81)} B r_{2}$ and ${ }^{(81,81)} B r_{2}$ have been calculated. By using both theory and experiment the radiative lifetime $\tau_{\text {rad. }}$ from B state to X state of ${ }^{(79,79)} B r_{2},{ }^{(79,81)} B r_{2}$ and ${ }^{(81,81)} B r_{2}$ for $v^{\prime}=14,15,17,18,19$ have been obtained. The predissociation of $B r_{2}$ in the $B^{3} \Pi_{o^{+}}{ }_{u}$ state is discussed.


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## Chapter 1

## Introduction

For a number of years the spectroscopy of halogen molecules, especially $I_{2}$, has attracted considerable interest. The spectrum of the B - X system of $I_{2}$ has been studied successfully and extensively by various research groups.

Bromine, being on the same column (VIIA) of the periodic table as iodine, has properties that closely resemble those of iodine. Of special spectroscopic interest is the B -X system of $B r_{2}$ which is very similar to the B - X system of $I_{2}$, the absorption and fluoresence spectra of both lying in the visible region. The $\mathrm{B}-\mathrm{X}$ system of $B r_{2}$ has also been extensively investigated $[5,9,10,19]$.

The bromine atom with atomic number 35 and international atomic weight of 79.909 a.m.u. has 35 electrons, 5 of which lie in the outermost, or valence, shell. The electronic configuration is expressed as

$$
\begin{array}{lllllllll}
\operatorname{Br}(35): & 1 s^{2} & 2 s^{2} & 2 p^{6} & 3 s^{2} & 3 p^{6} & 3 d^{10} & 4 s^{2} & 4 p^{5} \\
\text { or } & \mathrm{K} \mathrm{~L} \mathrm{M} & 4 s^{2} & 4 p^{5} & & & & &
\end{array}
$$

Bromine occurs natually in two isotopes, yielding three types of $B r_{2}$ which are ${ }^{79,79} \mathrm{Br}_{2},{ }^{79,81} \mathrm{Br} r_{2}$, and ${ }^{81,81} \mathrm{Br} r_{2}$ in a relative abundance of $1.0216: 2.0: 0.9784$.

The combination of two bromine atoms to form a molecule gives rise to a $X^{1} \Sigma_{o+u}$ ground state and the first excited state $B^{3} \Pi_{o+u}$ (see Figure 1.1) [24]. A few other states lying above the ground states are also shown in Figure 1.1.

Chapter II describes the theoretical work of dealing with the internal motion of a diatomic molecule. We consider molecular bromine as a non-translating rigid rotator


Figure 1.1: Potential energy curves for $B r_{2}$
and this rigid rotator moves around the center of mass which are the origins of both space and molecular coordinate system. We also consider the vibration as a simple harmonic motion. From the Born-Oppenheimer approximation, the wave function of the system can be separated to a good approximation into an electronic part $\psi_{e}$ and a vibrational part $\psi_{n}$ so that the coupled Schrödinger equation of the system be separated. From solving the two Schrödinger equations we can obtain the electronic and nuclear (vibrational and rotational) energies.

In fact, the vibration of molecule is a non-simple harmonic motion and the rotation of molecular bromine is not a rigid rotator. Therefore we have to amend the results obtained from the approximation to obtain finally the total energy of the system.

In Chapter III we describe the apparatus used to study the radiative lifetime of $B^{3} \Pi_{0^{+} u}$ state of $B r_{2}$ and the construction of bromine sample cell. We also report the absorption spectum in this chapter.

Chapter IV describes the procedure of analysing the data. We use the iodine atlas obtained by another research group [21] to calibrate the bromine spectrum. By checking the dispersion of each scan region we found the frequency of each absorption line. We used a digitizer to get two sets of data and then to calculate the area under each absorption line by using those data. In order to make sure the lines are not overlapped we assume the line is a Gaussian distrubution and then compare the two values of $\int k_{\nu} d \nu$ between the Gaussian distrubution and the real $\int k_{\nu} d \nu$. We also calculate the half width of each absorption spectral line to check whether the line is overlapped or not. In order to obtain the radiative lifetime we also calaulate the density of $B r_{2}$ in the different vibrational and rotational energy levels.

Chapter V provides a discussion of the results; we compare our results of radiative lifetime with the results obtained by other authors. The predissociation rate of molecular bromine in the $B^{3} \Pi_{0^{+} u}$ state is also discussed in this chapter.

## Chapter 2

## Theory

### 2.1 Internal motion of a diatomic molecule

An atom has only one nucleus and some electrons moving around it. Because the nucleus has much greater mass than the electrons, one can assume that all the electrons move approximately in a central potential produced by the nucleus and so estimate the energy levels. The simplest molecule consists of two atoms; for example, molecular bromine consists of two bromine atoms. The electrons in this kind of molecule move in the potential produced by the two nuclei, and nuclei will vibrate about their equilibrium positions (where the potential energy is at a minimum), and rotate around its center of mass. Therefore, both the electron and nuclear motions should be taken into account at the same time in the study of molecular internal motions. Because it has been found that there is a certain structure for every kind of molecule and this structure is determined by the equilibrium positions of nuclei, one can divide the molecular internal motion into three kinds: electronic motion, and rotational, vibrational motion of the nuclei.

Before we start to look these three kinds of motions, two kinds of coordinate systems should be introduced. One is the normal Cartesian system which will be fixed in space and will not move with molecule; another one is called the molecular coordinate system which will be fixed on the molecule (actually nuclei's equilibrium positions) and will rotate with the molecule (Fig.2.2). Both of the two systems will take the center of mass of the molecule as their origins. The relation between the two systems can be described


Figure 2.2: The Cartesian and Molecule Coordinate. Systems $\quad 0-x y z$ is the molecule coordinate systems $0-\xi \eta \zeta$ is the space coordinate systems
by the Eulerian angles ( $\phi, \theta, \delta$ ) [6].
For the molecular rotations, we can assume that each nucleus is fixed at its equilibrium position, the two nuclei can be recognized as a rigid rotor like a dumbell fixed on the $z$ axis of the molecular coordinate system (Fig.2.2). This "dumbell" can rotate freely around the original point (center of mass).

The vibrations can be described in the molecular coordinate system.

### 2.2 Born-Oppenheimer method

In quantum mechanics, the quantum states of a physical system are charaterized by a wave function, $\Psi$, which contain all the information about the physical system. The
probability of finding the system in such a state $\Psi$ is

$$
\begin{equation*}
|\Psi|^{2}=\int \Psi^{*} \Psi d \tau \tag{2.1}
\end{equation*}
$$

The dynamical evolution of the state vector $\Psi$ is governed by the Schrödinger equation:

$$
\begin{equation*}
i \hbar \frac{\partial \Psi}{\partial t}=H \Psi \tag{2.2}
\end{equation*}
$$

where $H$ is the Hamiltonian, an observable associated with the total energy of the system. That is,

$$
\begin{equation*}
H=T+U \tag{2.3}
\end{equation*}
$$

where $T$ and $U$ are the kinetic and potential energy of this dynamical system. The Hamiltonian of the $B r_{2}$ molecule can be expressed, to the first order, as [26]

$$
\begin{equation*}
H=\sum_{i=1}^{2} \frac{P_{i}^{2}}{2 M_{i}}+\sum_{j=1}^{Z_{1}+Z_{2}} \frac{p_{j}^{2}}{2 m_{i}}-\sum_{j=1}^{Z_{1}+Z_{2}} \frac{Z_{1} e^{2}}{r_{1 j}}-\sum_{j=1}^{Z_{1}+Z_{2}} \frac{Z_{2} e^{2}}{r_{2 j}}+\frac{Z_{1} Z_{2} e^{2}}{R_{12}}+\sum_{i>j} \frac{e^{2}}{r_{i j}} \tag{2.4}
\end{equation*}
$$

where
$Z_{1}, Z_{2}$ : atomic numbers of atom one and atom two
$\mathbf{P}_{\mathrm{i}}$ : the linear momentum of nucleus i
$p_{j}$ : the linear momentum of electron $j$
$M_{i}$ : the mass of nucleus i
$m_{i}$ : the mass of electron i
$r_{1 j}$ : the distance between nucleus 1 and electron j
$r_{2 j}$ : the distance between nucleus 2 and electron j
$R_{12}$ : the internuclear distance
$r_{i j}$ : the distance between electrons i and j

In the above equation, the first term describes the kinetic energy of the two bromine nuclei; the second term the electron kinetic energy; the third and the fourth are the coulomb potential energy between electrons and the nucleus one and nucleus two, respectively; the fifth term is the coulomb potential energy between the two nuclei; and the last term is the coulomb potential energy between all electrons.

In general, it is impossible to solve this Schrödinger equation exactly for such a system. Since the mass of electrons is much smaller than the mass of nucleus, the velocity of electron is much greater than that of nucleus. Whenever the nucleus moves a little bit, the electron has already moved through many orbits around it. Accordingly, Born and Oppenheimer introduced an approximation in which they separated the electronic and nuclear motions by supposing that the nuclei are fixed at their equilibrium positions and electrons move in a stable potential produced by the two nuclei, the distance between the two nuclei being regarded as a parameter. From solving the Schrödinger equation for the electrons, they could get the electron eigenenergy with the coordinate of nuclei as a parameter. Then, they solved the Schrödinger equation for the nuclear motions (i.e. vibrations and rotations) by substituting the electronic eigenenergy in.

In order to realize that, they wrote the wavefunction as,

$$
\begin{equation*}
\Psi=\psi_{e} \psi_{n} \tag{2.5}
\end{equation*}
$$

where $\psi_{e}$ is electronic eigenfunction and $\psi_{n}$ is the nuclear eigenfunction.
Substituting this eigenfuntion $\Psi$ into the Eqn.(2.2), we can get two equations:

$$
\begin{equation*}
\left[-\frac{\hbar^{2}}{2 m} \sum_{i} \nabla_{i}^{2}-\sum_{j=1}^{Z_{1}+Z_{2}} \frac{Z_{1} e^{2}}{r_{1 j}}-\sum_{j=1}^{Z_{1}+Z_{2}} \frac{Z_{2} e^{2}}{r_{2 j}}+\sum_{i>j} \frac{e^{2}}{r_{i j}}\right] \psi_{e}\left(R_{12}\right)=E_{e}\left(R_{12}\right) \psi_{e}\left(R_{12}\right) \tag{2.6}
\end{equation*}
$$

$$
\begin{equation*}
\left[-\sum_{j}^{2} \frac{\hbar^{2}}{2 M_{j}} \nabla_{j}^{2}+E_{e}\left(R_{12}\right)+\frac{Z_{1} Z_{2} e^{2}}{R_{12}}\right] \psi_{n}=E \psi_{n} \tag{2.7}
\end{equation*}
$$

When solving Eqn.(2.6), one can recognize $R_{12}$ as a parameter in the electronic eigenvalues and eigenfunctions. The third term of Eqn.(2.7) can be removed by supposing that it has be included in this parameter. Therefore the Eqn.(2.7) can be written as

$$
\begin{equation*}
\left[-\sum_{j}^{2} \frac{\hbar^{2}}{2 M_{j}} \nabla_{j}^{2}+E_{e}^{\prime}\left(R_{12}\right)\right] \psi_{n}=E \psi_{n} \tag{2.8}
\end{equation*}
$$

So, one can solve the Eqn.(2.6) to get a set of eigenvalues $E_{e}^{\mu}$ :

$$
\begin{equation*}
E_{e}^{\mu}=E_{e}^{\mu}\left(r_{i j}, R_{12}\right) \tag{2.9}
\end{equation*}
$$

and eigenfunctions $\psi_{e}^{\mu}$ :

$$
\begin{equation*}
\psi_{e}^{\mu}=\psi_{e}^{\mu}\left(r_{i j}, R_{12}\right) \tag{2.10}
\end{equation*}
$$

where $E_{e}^{\mu}\left(r_{i j}, R_{12}\right)$ and $\psi_{e}^{\mu}\left(r_{i j}, R_{12}\right)$ should be the sum of electronic kinetic and potential energy, and the electronic eigenfunctions for a certain molecular state.

It is quite obvious that in the Eqn. (2.8), the $E_{e}^{\prime}\left(R_{12}\right)$ actually takes the role of potential energy in the Schrödinger equation. It is well known that whenever the $E_{e}^{\prime}\left(R_{12}\right)$ has a minimum, there should be a stable structure corresponding to it. So, theoretically speaking, once one obtained $\psi_{e}^{\mu}\left(r_{i j}, R_{12}\right)$ and an electronic energy $E_{e}^{\mu}\left(r_{i j}, R_{12}\right)$, i.e. a stable molecular structure, from solving Eqn.(2.6), one can in principle determine the nuclear motion: vibrations and rotations, from Eqn.(2.8).

### 2.2.1 The vibration and rotation of diatomic molecules

In order to seperate the molecular vibrations and rotations, one can write down the Schrödinger Eqn.(2.3) in terms of a set of polar coordinates: $r, \theta$, and $\phi$ [6]

$$
\begin{equation*}
\left[T_{e}+T_{v}+T_{r}+U\left(R, x_{3}, y_{3}, z_{3}, \ldots x_{N}, y_{N}, z_{N}\right)-E_{r v e}\right] \Phi_{r v e}\left(R, \theta, \phi, x_{3}, \ldots z_{N}\right)=0 \tag{2.11}
\end{equation*}
$$

where $T_{e}$ is the electron kinetic energy operator,

$$
\begin{equation*}
T_{e}=-\frac{\hbar^{2}}{2 m} \sum_{i=3}^{N} \nabla_{i}^{2}-\frac{\hbar^{2}}{2 M_{N}} \sum_{i, j=3}^{N} \nabla_{i} \cdot \nabla_{j} \tag{2.12}
\end{equation*}
$$

where $M_{N}$ is the total nuclear mass, i.e.

$$
\begin{equation*}
M_{N}=m_{1}+m_{2} \tag{2.13}
\end{equation*}
$$

$T_{v}$ is the nuclear vibrational kinetic energy operator,

$$
\begin{equation*}
T_{v}=-\frac{\hbar^{2}}{2 \mu R^{2}} \frac{\partial}{\partial R}\left(R^{2} \frac{\partial}{\partial R}\right) \tag{2.14}
\end{equation*}
$$

where

$$
\begin{equation*}
\mu=\frac{m_{1} m_{2}}{m_{1}+m_{2}} \tag{2.15}
\end{equation*}
$$

while the $T_{r}$ is the nuclear rotational kinetic energy operator,

$$
\begin{equation*}
T_{r}=-\frac{\hbar^{2}}{2 \mu R^{2}}\left[\frac{1}{\sin ^{2} \theta}\left(\frac{\partial}{\partial \phi}+i \frac{L_{x}}{\hbar} \sin \theta-i \frac{L_{z}}{\hbar} \cos \theta\right)^{2}+\frac{1}{\sin \theta}\left(\frac{\partial}{\partial \theta}-i \frac{L_{y}}{\hbar}\right) \sin \theta\left(\frac{\partial}{\partial \theta}-i \frac{L_{y}}{\hbar}\right)\right] \tag{2.16}
\end{equation*}
$$

where $L_{x}, L_{y}$ and $L_{z}$ are the electron angular momentum operators in the molecular coordinate system.

From Eqn.(2.16), one can see that it is impossible to separate the electron and molecular coordinates except for neglecting $L_{x}, L_{y}$ and $L_{z}$. People usually neglect these angular momenta first, solve the simplified equations to get the electron, vibration and rotation energy, and then to discuss the coupling between these motions.

From Herzberg, for the first approximation (small rotation) the wavefunction of the system can be written as [17]

$$
\begin{equation*}
\Psi_{r v e}=\psi_{e} \cdot \frac{1}{R_{12}} \psi_{v}\left(R_{12}-R_{e}\right) \cdot \psi_{\tau} \tag{2.17}
\end{equation*}
$$

where $R_{e}$ is the distance between two nuclei at the equilibrium position.
$\Psi_{\text {rve }}$ in the above equation is called the rovibronic wavefunction.
The total energy of the system is

$$
\begin{equation*}
E_{t o t .}=E_{e}+E_{v}+E_{r} \tag{2.18}
\end{equation*}
$$

Eqn.(2.17) holds to a good approximation expect for the high vibrational and rotational energy levels of the molecule. When the vibrational quantum number, $v$, increases, the amplitude of the vibration will increase, while when the rotational quantum number, J , increases, the distance between the two nulei will increase. Therefore, we have to use the model of the anharmonic oscillator and consider the molecule as a non-rigid rotator.

After adding the potential of the anharmonic oscillator and the non-rigid rotator to the potential in Eqn.(2.8), we can ultimately obtain the rovibronic energy,

$$
\begin{align*}
E= & h c\left\{T_{e}+\left[\omega_{e}\left(v+\frac{1}{2}\right)-\omega_{e} x_{e}\left(v+\frac{1}{2}\right)^{2}+\ldots\right]+\left[B_{e}-\alpha_{e}\left(v+\frac{1}{2}\right)\right] J(J+1)\right. \\
& \left.+\left[D_{e}-\beta_{e}\left(v+\frac{1}{2}\right)\right] J^{2}(J+1)^{2}+\ldots\right\} \tag{2.19}
\end{align*}
$$

All the constants $\omega_{e}, \omega_{e} x_{e}, \alpha_{e}, \beta_{e} T_{e}, B_{e}, D_{e}$ can be obtain from [2,20]
An important property is

$$
B_{e} \ll \omega_{e} \ll T_{e}
$$

That means

$$
\Delta E_{e} \gg \Delta E_{v} \gg \Delta E_{r}
$$

From the above equation, it can be seen that the rotational energy levels are added to the vibrational energy levels, while the vibrational energy levels are added to the electronic energy levels.

### 2.3 Electronic states of a diatomic molecule

There is only an axial symmetry about the internuclear axis in a diatomic molecule. The constant of the motion is only the component of the electronic orbital angular momentum, $\mathbf{L}$, along internuclear axis. That component $\mathbf{M}_{\mathbf{L}}$ of $\mathbf{L}$ is called $\Lambda$ and $\Lambda=\left|M_{L}\right|[13]$. The value of $\Lambda$ corresponding to each electronic state of molecule are shown in following table

| The $\Lambda$ value: | 0 | 1 | 2 | $3 \ldots$ |
| :--- | :--- | :--- | :--- | :--- |
| The molecular state: | $\Sigma$ | $\Pi$ | $\Delta$ | $\Phi \ldots$ |

All the states except for $\Lambda=0$ are doubly degenerate because $M_{L}$ can have the two values $+\Lambda$ and $-\Lambda$.

The spin of an electron is not affected by the electronic field. There is a magneitic field along the internuclear axis. For states $\Lambda \neq 0$, the magneitic field causes a precession of $S$ about the internuclear axis with a constant component $\Sigma$,

$$
\begin{equation*}
\Sigma=S, S-1, \ldots,-S \tag{2.20}
\end{equation*}
$$

For each state $\Lambda$ the spin degeneracy is $2 \mathrm{~S}+1$.
The total electronic angular momentum (in units $\hbar$ ) along the internuclear axis is:

$$
\begin{equation*}
\Omega=|\Lambda+\Sigma| \tag{2.21}
\end{equation*}
$$

where
$\Lambda$ : the projection of $L$ along internucler axis
S: the electron spin
$\Sigma$ : the projection of $S$ along internucler axis
Each electronic state finally is labelled by

$$
{ }^{2 S+1} \Lambda_{|\Lambda+\Sigma|}
$$

### 2.4 Coupling of electronic motion and rotation

We consider the case where the interaction of nuclear and electronic motion is very weak and the electronic motion is coupled very strongly to the internuclear axis (Hund's case a), when the total angular momentum is:

$$
\begin{equation*}
J=\Omega+R \tag{2.22}
\end{equation*}
$$

where $R$ is the rotation of the nuclei. In this thesis we are interested in the cases in which $\Omega$ is equal to zero. Hence,

$$
\begin{equation*}
\mathbf{J}=\mathbf{R} \tag{2.23}
\end{equation*}
$$

### 2.5 The symmetry properties of a diatomic molecule

### 2.5.1 The symmetry of the electronic wavefunction

In a diatomic molecule, any plane through the internuclear axis is a plane of symmetry. So for a $\Sigma$ state ( $\Lambda=0$ ), the electronic wavefunction eighter remains unchanged (for a $\Sigma^{+}$state), or changes sign (for a $\Sigma^{-}$state) upon reflection through such a plane of symmetry.

### 2.5.2 $g$ and $u$ symmetry of electronic states

For homonuclear diatomic molecule the electronic wavefunction has a fixed parity. The wavefunction either remains unchanged (even or $g$ (gerade)) upon inversion or change sign (odd or u (ungerade)). Because only homonuclear molecules have the inversion symmetry property, so the subscripts $g$ and $u$ are applicable to only homonuclear molecules.

### 2.5.3 + , - parity of rotational states

Rotational levels have ' + ' or '-' parity depending on the symmetry of the total wavefunction with respect to inversion at the origin of a space coordinate system.

### 2.5.4 s and a symmetry of rotational states

$s$ (symmetry) and a(antisymmetry) refer to the symmetry of the total wavefuction on exchanging the two identical nuclei (where the nuclear spin has been omitted).

### 2.6 The selection rules of molecular bromine for transitions

The selection rules can be summerized as following [18]:

### 2.6.1 For the electronic transitions

For electric dipole transitions between the electronic states, the selection rules are:

$$
\begin{align*}
\Delta \Lambda & =0, \pm 1  \tag{2.24}\\
\Delta \Omega & =0, \pm 1  \tag{2.25}\\
\Delta \Sigma & =0  \tag{2.26}\\
\Sigma^{+} \longleftrightarrow \Sigma^{+} & \tag{2.27}
\end{align*}
$$

$$
\begin{align*}
\Sigma^{-} & \longleftrightarrow \Sigma^{-}  \tag{2.28}\\
g & \longleftrightarrow u \tag{2.29}
\end{align*}
$$

For the bromine molecule, the third selection rule (2.26) cannot be used at all. Because $B r_{2}$ is a heavy molecule, the interaction between $L$ and $S$ may be stronger than the interaction with the internuclear axis. $\Sigma$ is not a good quantum number any more, so that $\Delta \Sigma=0$ is no longer true.

### 2.6.2 For the vibrational transitions

For the transitions between the vibrational states, the selection rules are:

$$
\begin{equation*}
\Delta v=0, \pm 1, \pm 2, \ldots \tag{2.30}
\end{equation*}
$$

But in the electronic transition the intensity of the vibrational spectrum band is proportional to the Franck-Condon Factor (F.C.F.). (See appendix B)

### 2.6.3 For the rotational transitions

The selection rules for the transitions between the rotational states of a homonulear molecule are:

$$
\begin{gather*}
\Delta J= \pm 1  \tag{2.31}\\
+\longleftrightarrow-  \tag{2.32}\\
s \longleftrightarrow s  \tag{2.33}\\
a \longleftrightarrow a \tag{2.34}
\end{gather*}
$$

From Eqn (2.31) we can obtain

P branch:

$$
\begin{equation*}
J^{\prime}=J^{\prime \prime}-1 \tag{2.35}
\end{equation*}
$$

and R branch:

$$
\begin{equation*}
J^{\prime}=J^{\prime \prime}+1 \tag{2.36}
\end{equation*}
$$

where the single prime and double prime represent the excited state and initial state, respectively.

### 2.7 The distribution of the number of molecules

Bromine molecules may exist in a variety of different states, each of which may be described by rotational, vibrational and electronic quantum numbers. When a molecular gas is at thermal equilibrium, the number of molecules in each state obeys the Boltzmann distribution:

$$
\begin{equation*}
N_{i}=N_{0} e^{-\beta E_{i}} \tag{2.37}
\end{equation*}
$$

where
$N_{i}$ is the number of molecules in state i
$N_{0}$ is the total number of molecules
$E_{i}$ is the energy of state of i relative to the lowest state
$\beta:(k T)^{-1}$
k is the Boltzmann constant
T is the temperature

If a state has degeneracy $g_{i}$, then the Boltzmann law becomes:

$$
\begin{equation*}
N_{i}=N_{0} g_{i} e^{-\beta E_{i}} \tag{2.38}
\end{equation*}
$$

We can apply the Boltzmann law to rotation, vibrational and electronic energy levels in turn. Because the energy separations of electron levels is much bigger than the one of vibrational and rotational levels, we can think that molecules stay in the electronic ground state at room temperature.

### 2.8 The effect of nuclear spin

There is a further symmetry property which must be considered, and which turns out to have very important implications for the population of different rotational levels. This symmetry property is the behaviour of the total wavefunction when equivalent nuclei are interchanged. As is known, nuclei with integer spin obey Bose-Einstein statistics, according to which the total wavefunction must be symmetric with respect to exchange of identical nuclei. Nuclei with half-integer spin obey Fermi-Dirac statistics, according to which the total wavefunction is antisymmetric with respect to exchange of nuclei. For $B r_{2}$, exchange of nuclei leaves the electronic wavefunction unchanged. The vibrational wavefunction is also unchanged on nuclear exchange, because the vibrational wavefunction only deponds on the magnitude of the bond length. But, the nuclear exchange influences the rotational wavefunction. Rotational wavefunctions are symmetric if J is even and are antisymmetric if $J$ is odd. The bromine nucleus has spin $I$, the degeneracy introduced by nuclear spin is shown in table 2.1

The intensity of spectral lines are propotional to degeneracy. The neighbouring spectral lines in the same $P$ branch and $R$ branch will have symmetry and antisymmetry, respectively. When the nuclear spin $I$ is equal to a integer, the ratio of the intensity of

Table 2.1: The degeneracy introduced by nuclear spin

| Nuclear spin | Integer |  | Half-integer |  |
| :--- | :--- | :--- | :--- | ---: |
| $\Psi_{\text {rve }}$ | s | a | s | a |
| Degeneracy | $(\mathrm{I}+1)(2 \mathrm{I}+1)$ | $\mathrm{I}(2 \mathrm{I}+1)$ | $(\mathrm{I}+1)(2 \mathrm{I}+1)$ | $\mathrm{I}(2 \mathrm{I}+1)$ |

neighbour spectral lines is

$$
\begin{equation*}
\frac{I_{a}}{I_{s}}=\frac{I}{I+1} \tag{2.39}
\end{equation*}
$$

When I has a half-integral value, we have

$$
\begin{equation*}
\frac{I_{a}}{I_{s}}=\frac{I+1}{I} \tag{2.40}
\end{equation*}
$$

Where the subscript $s$ indicates a symmetric and a indicates an antisymmetric state. The nuclear spin, $I$, of each bromine atom is $\frac{3}{2}$. So, the total nuclear spin, $I=I_{1}+I_{2}$, is 0,1,2,3.

In the ground electronic state, $X^{1} \Sigma_{0^{+} g}$, bromine molecules with odd J values are referred to as ortho-bromine and those with even J values as para-bromine. For odd J (ortho), we have $I=1(2 \mathrm{I}+1=3$ states) and $I=3(2 \mathrm{I}+1=7$ states), i.e. totally we have 10 antisymmetric states. For even J (para), we have $I=0(2 \mathrm{~J}+1=1$ state $)$ and $I=2(2 \mathrm{~J}+1=5$ states $)$, i.e. we totally have 6 symmetric states. Hence the hyperfine partition factor is $\frac{10}{16}=\frac{5}{8}$ for ortho states, and $\frac{6}{16}=\frac{3}{8}$ for para states.

Thus, at room temperature, we can get the number of moleculer per $\mathrm{cm}^{3}$ in a particular vibrational and rotational states.

The density of ortho state of (odd J) ${ }^{(79,79)} B r_{2}$ and ${ }^{(81,81)} B r_{2}$ satisfies Eqn.(2.41), and para state (even J) of ${ }^{(79,79)} B r_{2}$ and ${ }^{(81,81)} B r_{2}$ satisfies Eqn.(2.42). (For more details see appendix C)

$$
\begin{align*}
N_{m v^{\prime \prime} J^{\prime \prime}=}= & \frac{N_{0}}{V} \times M \\
& \times \frac{e^{-\beta E_{v} \prime \prime}}{\sum_{v} v^{\prime \prime} e^{-\beta E_{v^{\prime \prime}}}} \times \frac{5}{4} \frac{\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}}}{\sum_{J^{\prime \prime}}\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}}} \times e^{-\beta E_{e}}  \tag{2.41}\\
N_{m v^{\prime \prime} J^{\prime \prime}=}= & \frac{N_{0}}{V} \times M \\
& \times \frac{e^{-\beta E_{v^{\prime \prime}}}}{\sum_{v^{\prime \prime}} e^{-\beta E_{v} \prime \prime}} \times \frac{3}{4} \frac{\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}}}{\sum_{J^{\prime \prime}}\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}}} \times e^{-\beta E_{e}} \tag{2.42}
\end{align*}
$$

where the sum over $J^{\prime \prime}$ is from 0 to infinit.
There are no para and ortho states defined for ${ }^{(79,81)} B r_{2}$ where the two nuclei are inequivalent. The density of ${ }^{(79,81)} B r_{2}$, at room temperature, satisfies Eqn.(2.43)

$$
\begin{align*}
N_{m v^{\prime \prime} J^{\prime \prime}}= & \frac{N_{0}}{V} \times M \times \frac{e^{-\beta E_{v} \prime \prime}}{\sum_{v^{\prime \prime}} e^{-\beta E_{v^{\prime \prime}}}} \times \\
& \frac{\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}}}{\sum_{J^{\prime \prime}}\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}} \times e^{-\beta E_{e}}} \tag{2.43}
\end{align*}
$$

where $J^{\prime \prime}$ includes odd $J^{\prime \prime}$ and even $J^{\prime \prime}$.
$M$ is the fractional abundances of the type of molecule studied, where $M$ is equal to 0.2554 for ${ }^{(79,79)} B r_{2}, 0.2446$ for ${ }^{(81,81)} B r_{2}$ and 0.5 for ${ }^{(79,81)} B r_{2}$.

For the ground electronic state $E_{e}$ is equal to zero.
The partition function $\frac{e^{-\beta E_{v} \prime \prime}}{\sum_{v^{\prime \prime}} e^{-\beta E_{v^{\prime \prime}}}}$ is the probability of molecules in vibrational states.

$$
\begin{equation*}
\frac{N_{0}}{V}=\frac{P}{R T}=2.08 \times 10^{17}\left(\text { molecules } / \mathrm{cm}^{3}\right) \tag{2.44}
\end{equation*}
$$

P : pressure in the cell
R : molar gas constant
T : room temperature


Figure 2.3: The absorption of radiation

### 2.9 Absorption of light by a diatomic molecule

### 2.9.1 Definition of the absorption coefficient

When a beam of light is sent through a bromine gas cell the intensity of the transmitted light, $I_{\nu}$, may show a frequency distribution similar to the one depicted in Figure 2.3.[23] where $\nu_{0}$ is the frequency at the centre of the line.

In general, the absorption coefficient $k_{\nu}$ of the gas, is defined by the equation

$$
\begin{equation*}
I_{\nu}=I_{0} e^{-k_{\nu} L} \tag{2.45}
\end{equation*}
$$

that is,

$$
\begin{equation*}
k_{\nu}=(1 / L) \ln \left(I_{0} / I_{\nu}\right) \tag{2.46}
\end{equation*}
$$

where
$I_{0}$ is the intensity incident on the cell
L is the length of the cell

When L is meassured in $\mathrm{cm}, k_{\nu}$ is expressed in $\mathrm{cm}^{-1}$, and $\nu$ is the wavenumber of the radiation in $\mathrm{cm}^{-1}$. From Fig. 2.3 and Eqn.(2.46), we have a curve in Figure 2.4 [23].


Figure 2.4: The typical shape of a spectral line
where $\Delta \nu$ is called the half-width of the absorption line.
2.9.2 The relations between the Einstein coefficients and the integrated absoption coefficient

The intensity of an absorption line can be defined by equation [13]

$$
\begin{equation*}
I_{\nu}^{n m}=I_{0}^{n m} N_{m} B_{n m} h \nu_{n m} L \tag{2.47}
\end{equation*}
$$

where
m is initial(lower energy) state
n is excited(higher energy) state
$N_{m}$ is the number of molecule per $\mathrm{cm}^{3}$ in the initial state m
$B_{n m}$ is the Einstein transition probability of absorption
$\nu_{n m}$ is the transition frequency

The intensity of a spectral line in emission is written as

$$
\begin{equation*}
I_{\nu^{\prime}}^{n m}=N_{n} h c \nu_{n m} A_{n m} \tag{2.48}
\end{equation*}
$$

where c is the speed of light and $A_{n m}$ is the Einstein transition probability of spontaneous emission.

From wave mechanics [13], we find for transitions between non-degenerate levels is

$$
\begin{equation*}
A_{n m}=\frac{64 \pi^{4} \nu_{n m}^{3}}{3 h}\left|\mathbf{R}^{n m}\right|^{2} \tag{2.49}
\end{equation*}
$$

and

$$
\begin{equation*}
B_{m n}=\frac{8 \pi^{3}}{3 h^{2} c}\left|\mathbf{R}^{\mathrm{nm}}\right|^{2} \tag{2.50}
\end{equation*}
$$

where $\mathbf{R}^{\mathbf{n m}}$ is a transition dipole moment.
so,

$$
\begin{equation*}
A_{n m}=8 \pi h \nu_{n m}^{3} B_{m n} \tag{2.51}
\end{equation*}
$$

For the case of a transition between the two levels $n$ and $m$ of degeneracy $d_{n}$ and $d_{m}$, respectively, we have

$$
\begin{gather*}
A_{n m}=\frac{64 \pi^{4} \nu_{n m}^{3}}{3 h d_{n}} \sum_{m_{J^{\prime \prime}}}\left|\mathbf{R}^{\mathrm{n}_{\mathbf{J}^{\prime}} \mathrm{m}_{\mathbf{J}^{\prime \prime}}}\right|^{2}  \tag{2.52}\\
B_{m n}=\frac{8 \pi^{3}}{3 h^{2} c d_{m}} \sum_{m_{J^{\prime \prime}}}\left|\mathbf{R}^{\mathrm{n}_{\mathbf{J}^{\prime}} \mathrm{m}_{\mathbf{J}^{\prime \prime}}}\right|^{2}  \tag{2.53}\\
A_{n m}=\frac{d_{m}}{d_{n}} 8 \pi h c \nu_{n m}^{3} B_{m n} \tag{2.54}
\end{gather*}
$$

Because the absorption coefficient $k_{\nu}$ varies across an absorption line (or band), the light absorbed by the transition $n-m$ for a small $\Delta L$ is given by [16]

$$
\begin{equation*}
I_{a b s .}^{n m}=\int\left(I_{\nu}^{0}-I_{\nu}\right) d \nu=I_{\nu}^{0} \Delta L \int k_{\nu} d \nu \tag{2.55}
\end{equation*}
$$

where the incident intensity $I_{\nu}^{0}$ is assumed to be constant over the width of the line or band. Substituting Eqn.(2.47) into the above equation and taking $I_{0}^{n m}$ as $I_{\nu}^{0}$ we obtain for the integrated absorption coefficient

$$
\begin{equation*}
\int k_{\nu} d \nu=N_{m} B_{m n} h \nu_{n m} \tag{2.56}
\end{equation*}
$$

2.9.3 The relation between the Einstein coefficient and transition probabilities

From Herzberg [15], the transition probability $B_{m n, v^{\prime \prime} v^{\prime}, J^{\prime \prime} J^{\prime}}$ for absorption is given by

$$
\begin{equation*}
B_{m n, v^{\prime \prime} v^{\prime}, J^{\prime \prime} J^{\prime}}=\frac{8 \pi^{3}}{3 h^{2} c}\left|\mathbf{R e}_{\mathrm{e}}^{\mathrm{nm}}\right|^{2}\left|\mathbf{R}_{\mathrm{vib} .}^{\mathrm{v}^{\prime} \mathrm{v}^{\prime \prime}}\right|^{2} \frac{\sum_{\mathrm{M}^{\prime} \mathrm{M}^{\prime \prime}}\left|\mathbf{R}_{\mathrm{rot}}^{\mathrm{J}^{\prime} \mathrm{J}^{\prime \prime}}\right|^{2}}{2 \mathrm{~J}^{\prime \prime}+1} \tag{2.57}
\end{equation*}
$$

where the total matrix element $R^{n m}$ for the system is

$$
\begin{equation*}
R^{\mathrm{nm}}=\mathbf{R}_{\mathrm{e}}^{\mathrm{nm}} \mathbf{R}_{\mathrm{vib}}^{v^{\prime} \mathrm{v}^{\prime \prime}} \mathbf{R}_{\text {rot. }}^{\mathrm{J}^{\prime} \mathrm{J}^{\prime \prime} .} \tag{2.58}
\end{equation*}
$$

and the summation is over all values of the magnetic quantum numbers $M^{\prime}$ and $M^{\prime \prime}$ of upper and lower states.

The electronic transition probability is given by

$$
\begin{equation*}
\left|\mathbf{R}_{\mathrm{e}}^{\mathrm{mn}}\right|^{2}=\left|\int \psi_{\mathrm{e}^{*}} \mathrm{M}_{\mathrm{e}} \psi_{\mathrm{e}^{\prime \prime}} \mathrm{d} \tau_{\mathrm{e}}\right|^{2} \tag{2.59}
\end{equation*}
$$

where $M_{e}$ is the electric moment which only depends on the electrons.

The vibrational transition probability is given by

$$
\begin{equation*}
\left|\mathbf{R}_{\mathbf{v i b}^{v^{\prime}} \mathbf{v}^{\prime \prime}}\right|^{2}=\left|\int \psi_{\mathbf{v}^{*}}^{*} \psi_{\mathbf{v}^{\prime \prime}} \mathrm{dr}\right|^{2}=\left|\left\langle\mathrm{v}^{\prime} \mid \mathbf{v}^{\prime \prime}\right\rangle\right|^{2} \tag{2.60}
\end{equation*}
$$

The $\left|\left\langle v^{\prime} \mid v^{\prime \prime}\right\rangle\right|^{2}$ is the well-known Franck-Condon Factor (F.C.F.) for the transition $v^{\prime}-v^{\prime \prime}$ (see appendix B). Usually people use the symbol

$$
\begin{equation*}
q_{v^{\prime}, v^{\prime \prime}}=\left|<v^{\prime}\right| v^{\prime \prime}>\left.\right|^{2} \tag{2.61}
\end{equation*}
$$

## The rotational transition probability

For rotational transition probability we have to consider three directions, $x, y$, and $z$, in space coordinate system. For example, the transition probability in the $z$ direction is

$$
\begin{equation*}
\left|\mathbf{R}_{\text {rot. }}^{\mathbf{J} \mathbf{J}^{\prime \prime}}\right|^{2}=\left|\int \sin \theta \cos \theta \psi_{\mathbf{r}^{*}}^{*} \psi_{\mathbf{r}^{\prime \prime}} \mathrm{d} \theta \mathrm{~d} \phi\right|^{2} \tag{2.62}
\end{equation*}
$$

In appendix $A$, we have shown the derivation of these three equations in detail. The F.C.F. and rotational part are given in appendix B.

We used both theory and experiment to obtain the electronic transition probability. $\left|\mathbf{R}_{\mathbf{e}}\right|^{\mathbf{2}}$ is a more fundamental measure of the transition probability. From Eqn.(2.56) and (2.57), we can get
where $\nu_{n m}$ is in wavenumber units.

### 2.9.4 The radiative lifetime of $B^{3} \Pi_{0+u}$ state of $B r_{2}$

The radiative lifetime of an molecule in a definite excited electronic state $n$ can be calculated theoretically. We have in general,

$$
\begin{equation*}
\tau_{\text {rad. }}=\frac{1}{\sum_{m} A_{n m}} \tag{2.64}
\end{equation*}
$$

The radiative lifetime of rovibronic levels in the $B^{3} \Pi_{0^{u}}$ state of molecular bromine is:

$$
\begin{equation*}
\tau_{\text {rad. }}=\frac{1}{\sum_{v^{\prime \prime}, J^{\prime \prime}} A_{v^{\prime} v^{\prime \prime}, J^{\prime} J^{\prime \prime}}} \tag{2.65}
\end{equation*}
$$

where $A_{v^{\prime}, v^{\prime \prime}, J^{\prime}, J^{\prime \prime}}$ is the Einstein coefficient for spontaneous emission from the state $J^{\prime}$ which is in the $v^{\prime}$ state into the state $J^{\prime \prime}$ of $v^{\prime \prime}$ state. $\tau_{\text {rad. }}$ varies with $v^{\prime}$ and this variation can be substantial over the whole vibrational energy range of an electronically-excited manifold.

In order to compare the magnitudes of $\tau_{\text {rad }}$. obtained for different $v^{\prime}$ levels in various investigations, it is desirable first to transform from $\tau_{R}$ values into the corresponding electronic transition probability $\left|\mathbf{R}_{\mathrm{e}}\right|^{2}$. In the Born-Oppenheimer approximation, $\left|R_{e}\right|^{2}$ is a strictly electronic transition probability and the vibrational and rotationalenergy dependences of $\tau_{\text {rad. }}$ are factored out by the transformation from $\tau_{\text {rad. }}$ to $\left|\mathbf{R}_{\mathbf{e}}\right|^{\mathbf{2}}$. The expression of $\tau_{\text {rad. }}$ is as follows [8],

$$
\begin{equation*}
\tau_{\text {rad. }}=\frac{1}{\sum_{v^{\prime \prime}} A_{v^{\prime}, v^{\prime \prime}}}=\frac{3 h \cdot d_{n}}{64 \pi^{4} \cdot d_{m} \sum_{v^{\prime \prime}} q_{v^{\prime} v^{\prime \prime} \nu^{3}\left|\mathbf{R}_{\mathrm{e}}\right|^{2} \frac{\sum_{\mathbf{J}^{\prime \prime}} \mid \mathbf{R}_{\text {rot }}^{\left.\mathbf{J}^{\prime} \mathbf{J}^{\prime \prime}\right|^{2}}}{2 \mathbf{J}^{\prime \prime}+1}}} \tag{2.66}
\end{equation*}
$$

From the absorption spectrum we can get the value of $\left|\mathbf{R}_{e}\right|^{2}$ by using Eqn.(2.63). Also we know that $\frac{d_{m}}{d_{n}}=1$ in our case and the rotation part of Eqn.(2.66) when the $P$ and R branches are considered together is equal to 1 (see appendix B ), so we finally can obtain the Eqn.(2.67),

$$
\begin{equation*}
\tau_{\text {rad. }}=\frac{3 h}{64 \pi^{4}\left|\mathbf{R}_{\mathbf{e}}\right|^{2} \sum_{\mathbf{v}^{\prime \prime}} \mathbf{q}_{\mathbf{v}^{\prime} \mathbf{v}^{\prime \prime} \nu^{3}}} \tag{2.67}
\end{equation*}
$$

In our case, it is possible to calculate a $\tau_{\text {rad }}$. value for $v^{\prime}=14,15,17,18,19$ by using the $\left|\mathbf{R e}_{\mathrm{e}}\right|^{2}$ values obtained from theory and experiment.

### 2.9.5 The predissociation of $B r_{2}$ in the $B^{3} \Pi_{0^{+} u}$ state

From Fig. 1.1 one can see that there is a crossing point between the excited state $B^{3} \Pi_{0+u}$ and the unbound state ${ }^{1} \Pi_{1 u}$. The vibrational energy levels of the the $B^{3} \Pi_{o+u}$ near the crossing point have a higher probability of producing a non-radiative transition to the ${ }^{1} \Pi_{1 u}$ state; then the atoms will separate, the entire process being called predissociation.

The density of molecular bromine in the excited states, $N^{*}$, changing with time, can be written as [4]

$$
\begin{equation*}
\frac{d N^{*}}{d t}=B_{N N^{*}} \cdot I_{\text {laset }} \cdot\left(N-N^{*}\right)-\left(\Gamma_{R}+\Gamma_{P}+\Gamma_{C}\right) \cdot N^{*} \tag{2.68}
\end{equation*}
$$

Where

$$
B_{N N} \cdot I_{\text {laser }}: \text { the laser' excitation rate }
$$

N : the density of $B r_{2}$ in the ground state
$\Gamma_{R}:$ the radiative decay rate $\left(\Gamma_{R}=\frac{1}{\tau_{\text {rad. }}}\right)$
$\Gamma_{P}$ : the predissociation rate
$\Gamma_{C}$ : the collisional decay rate

Taking $\frac{d N^{*}}{d t}=0$, we can get

$$
\begin{equation*}
N^{*}=\frac{B_{N N^{*}} I_{\text {laser }} N}{B_{N N^{*}} I_{\text {laser }}+\Gamma_{R}+\Gamma_{P}+\Gamma_{C}} \tag{2.69}
\end{equation*}
$$

For iodine,

$$
\begin{equation*}
\Gamma_{P}=k_{v^{\prime}} J^{\prime}\left(J^{\prime}+1\right)+a_{v^{\prime}}^{2} \tag{2.70}
\end{equation*}
$$

One can model bromine in the same way.
The fluoresence intensity, $I_{F}$, is proportional to $N^{*}$. So, one knows that
$\frac{1}{I_{F}} \propto J^{\prime}\left(J^{\prime}+1\right)$

One can draw a graph of $\frac{1}{I_{F}}$ vs. $J^{\prime}\left(J^{\prime}+1\right)$ to measure the predissociation rate, $\Gamma$.

## Chapter 3

## Experimental apparatus and spectrum

In this chapter we describe the apparatus used to measure the radiative lifetime of the $B^{3} \Pi_{0+u}$ state of $B r_{2}$ molecule.

### 3.1 Preparation of the sample cell

A pyrex sample cell, of length $14.09 \pm 0.05 \mathrm{~cm}$, was continuously heated and evacuated to a background pressure of $3.8 \times 10^{-6}$ torr. Part of the vacuum system was also cooled with liquid nitrogen. The sample cell was filled with dry $B r_{2}$ vapour, and a mixed methanol and liquid nitrogen bath was used to cool the liquid bromine to a temperature of $-(32.5 \pm 0.2)^{\circ} \mathrm{C}$. This environment was maintained for about ten mintues to allow bromine vapour to diffuse into the sample cell. The molecules were contained in T-shape pyrex sample cell, filled with isotopic bromine (79-79), (79-81), (81-81) whose relative abundances were $1.0216: 2.0: 0.9784$, respectively. The sample cell was then sealed and removed from the vacuum system. Under these conditions the $B r_{2}$ pressure inside the sample cell was $3.6 \pm 0.2$ torr, which was sufficient to obtain a peak absorption of about $30 \%$ for the rotational lines of bromine molecule under study. For stronger absorption, we could increase the pressure of the sample cell. Then, the collisions probability among bromine molecules will increase; this is a method of broadening the absorption line.

Using the same techniques we can prepare an iodine sample cell. The spectrum of the B-X system of $I_{2}$ has been studied successfully and extensively by various research groups. Therefore we can use a $I_{2}$ sample cell to get the fluorescence spectrum of $I_{2}$ and


Figure 3.5: Experimental arrangment. $\quad M_{1}, M_{2}$ : total reflectional mirror; $S$ : splitter; $F_{1}, F_{2}, F_{3}, F_{4}, F_{5}$ : filter; PM: photomultiplier; PD: photodiode; MC: monochrameter; PC: photo counter; TLR1,TLR2: two line recorder
then we can use the $I_{2}$ fluorescence spectrum obtained by [21] to calibrate the spectrum of $B r_{2}$.

### 3.2 Experimental set-up

A block diagram of the experimental arrangement used for measuring the lifetime of the $B^{3} \Pi_{0^{+} u}$ state of $B r_{2}$ is shown in figure 3.5.

A Coherent CR-15 SG argon ion laser tuned to the $5145 \AA$ line, and an output power of 6 W was used to pump a Cohererent CR-699-21 scanning dye laser. The dye
laser, using Rhodamine 6 G dye, gave a peak output power of 800 mW . This dye laser was connected to an electronic scanning system capable of tuning the laser at different scan speeds. In our experiment we tuned the dye laser from approximately $17464 \mathrm{~cm}^{-1}$ to $17480 \mathrm{~cm}^{-1}$, with the electronic scanner set to scan a $30 \mathrm{GHz}\left(\simeq 1 \mathrm{~cm}^{-1}\right.$ ) region per scan period of 5 minutes. This allowed us to excite the specific rovibrational levels ( $v^{\prime}, J^{\prime}$ ) of $B r_{2} B^{3} \Pi_{0^{+}}$state from the $X^{1} \Sigma_{0^{+} g}$ ground state. The dye laser beam was split into two by a beam splitter S . One of the beams was passed through the $B r_{2}$ sample cell while the other was directed through an $I_{2}$ sample cell. Less than 1 mW intensity of the beam was going into the $\mathrm{Br}_{2}$ sample cell. The beam area $3.14 \mathrm{~mm}^{2}$. The spectrum of iodine, which has already been studied extensively by other research groups, served as a reference for calibration. Both, absorption and fluorescence spectra were recorded for $B r_{2}$, whereas, only the fluoresence spectrum was recorded for $I_{2}$. A photodiode (HP PIN 5082-4220) and two photomultipliers (EMI 9558 B, EMI 9558 QB) were used as detectors for absorption and fluorescence, respectively. Several glass color filters were used in the path of the dye laser beam to reduce the intensity of the beam before it entered the sample cells and the detectors, in order to avoid saturation. Two double line recorders (PM 8252A) were used for recording purpose. One was used to record simultaneously the fluorescence spectra of $B r_{2}$ and $I_{2}$ with the other used to trace the absorption spectrum of $B r_{2}$ and the fluorescence spectrum of $I_{2}$. A monochrometer was used as an aid to obtain the accurate frequencies which were needed during the experiment.

### 3.3 Absorption spectrum of molecular bromine



Figure 3.6: Part of the Absorption Spectrum

## Chapter 4

Data Analysis

### 4.1 Assignment of $B r_{2}$ lines

An arbitrary zero on the horizontal axis of the spectrum was established. The distance to each $I_{2}$ fluoresence peak was measured and the frequency $\nu_{I_{2}}$ in $\mathrm{cm}^{-1}$ was plotted against the distance d in cm . From this graph we can find the slope, a, and the intercept b on each scan of the laser. If $\nu$ vs. $d$ is linear then an average dispersion can be taken and we can use this dispersion a to find the frequency $\nu_{B r_{2}}$ on each $B r_{2}$ line which is

$$
\begin{equation*}
\nu_{B r_{2}}=a d^{\prime}+b^{\prime} \tag{4.71}
\end{equation*}
$$

where $d^{\prime}$ is the distance from an arbitrary zero on the horizontal axis to each $B r_{2}$ absorption line, and $b^{\prime}$ is the intercept for $B r_{2}$ lines on each scan of dye laser, that is

$$
\begin{equation*}
b^{\prime}=b+0.428 a \tag{4.72}
\end{equation*}
$$

where the number 0.428 is the separation distance between $I_{2}$ and $B r_{2}$ lines. (Because the two line recorder (PM 8252A) has a fixed separation between the two pens)

Using Eqn.(4.71) we obtained the frequencies of all the absorption lines from the experimental data. Then all these frequencies were compared with theoretical ones calculated using Eqns.(4.73) and (4.74). The difference between the two values should vary smoothly and in the same direction.

Here we gave a example, ${ }^{(79,79)} B r_{2}$, band $15^{\prime}-1^{\prime \prime}$ in table 4.2

Table 4.2: Obtaining the band $15^{\prime}-1^{\prime \prime}$ of ${ }^{(79,81)} B r_{2}$

| line no. | $\mathrm{R}(\mathrm{J}), \mathrm{P}(\mathrm{J})$ | $\mu\left(\mathrm{cm}^{-1}\right)$ | $\nu\left(\mathrm{cm}^{-1}\right)$ | $\nu-\mu$ |
| :--- | :--- | :---: | :---: | :---: |
| 195 | $\mathrm{R}(58)$ | 17478.7155 | 17478.691 | -0.025 |
| 153 | $\mathrm{R}(59)$ | 17475.1262 | 17475.099 | -0.027 |
| 102 | $\mathrm{R}(60)$ | 17471.4733 | 17471.445 | -0.028 |
| 50 | $\mathrm{R}(61)$ | 17467.7568 | 17467.732 | -0.025 |
| 188 | $\mathrm{P}(55)$ | 17478.1605 | 17478.132 | -0.029 |
| 149 | $\mathrm{P}(56)$ | 17474.5676 | 17474.530 | -0.038 |
| 92 | $\mathrm{P}(57)$ | 17470.9113 | 17470.882 | -0.029 |
| 42 | $\mathrm{P}(58)$ | 17467.1916 | 17467.161 | -0.031 |

In the table $4.2 \mu$ and $\nu$ are theoretical and experimental frequencies, respectively.

### 4.2 Calculating the $B r_{2}$ transition energies

The transition energies for ${ }^{79,79} \mathrm{Br}_{2}$ and ${ }^{81,81} \mathrm{Br}_{2}$ can be calculated by using the following formula:

$$
\begin{gather*}
E_{X-\text { state }}=T_{v^{\prime \prime}}+B_{v^{\prime \prime}}\left(J^{\prime \prime}\left(J^{\prime \prime}+1\right)\right)-D_{v^{\prime \prime}}\left(J^{\prime \prime}\left(J^{\prime \prime}+1\right)\right)^{2}+H_{v^{\prime \prime}}\left(J^{\prime \prime}\left(J^{\prime \prime}+1\right)\right)^{3}  \tag{4.73}\\
E_{B-\text { state }}=T_{v^{\prime}}+B_{v^{\prime}}\left(J^{\prime}\left(J^{\prime}+1\right)\right)-D_{v^{\prime}}\left(J^{\prime}\left(J^{\prime}+1\right)\right)^{2}+H_{v^{\prime}}\left(J^{\prime}\left(J^{\prime}+1\right)\right)^{3} \tag{4.74}
\end{gather*}
$$

Where
$T_{v}=T_{v, J=0}$ is the vibrational term value relative to $X^{1} \Sigma_{0+g}$ state.
The energy is measured in wave number $\left(\mathrm{cm}^{-1}\right)$ units and the $X \rightarrow B$ transitions for the P and R branches in ${ }^{(79,79)} B r_{2}$ and ${ }^{(81,81)} \mathrm{Br}_{2}$ were calculated. The constants, $T_{v}, B_{v}, D_{v}$, and $H_{v}$ were obtained from [2]. For ${ }^{(79,81)} B r_{2}$, the transition energies were calculated by averaging the results of ${ }^{(79,79)} B r_{2}$ and ${ }^{(81,81)} B r_{2}$.

### 4.3 The absorption band strengths

From Eqn.(2.41),(2.42) and (2.43) we can obtain the number of bromine molecules in each rotational state of each vibrational state. (The probability of being in a vibrational state is estimated by summation from $v=0$ to $v=10$. The probability of being in a rotational state is integrated from $J=0$ to $J=\infty$ for both R branch and P branch). At room temperature, the B-state levels are sparsely populated so only the X -state levels need te be calculated. From calculating the partition function $\frac{e^{-\beta v_{v} \prime \prime}}{\sum_{v^{\prime \prime}} e^{-\beta E v^{\prime \prime}}}$, one can assume that most bromine molecules occupy the states $v^{\prime \prime}=0,1$ and 2 only.

From Eqn.(2.38), the Boltzmann distribution law for rotational levels is now [22]

$$
\begin{equation*}
N_{J^{\prime \prime}} \cong N_{0}\left(2 J^{\prime \prime}+1\right) e^{-\beta B_{v} J^{\prime \prime}\left(J^{\prime \prime}+1\right)} \tag{4.75}
\end{equation*}
$$

The particle density will not be affected by nuclear spin.
By differentiation Eqn.(4.75) it can be shown that the quantum number of the state with the greatest population is

$$
\begin{equation*}
J_{\max }=\sqrt{2 \beta B_{v}}-\frac{1}{2} \tag{4.76}
\end{equation*}
$$

Taking the value of $B_{v} \cong 0.08 \mathrm{~cm}^{-1}$ [2], we can obtain

$$
\begin{equation*}
J_{\max } \cong 35 \tag{4.77}
\end{equation*}
$$

In the table 4.4 we gave the part of particle densities on para and ortho states of $v^{\prime \prime}=1$. The constants used for calculating the particle density are shown in table 4.3 [2].

Franck-Condon factors gives an approximation to the relative intensities. A chart of F.C.F.'s for $0 \leq v^{\prime} \leq 48$ to $0 \leq v^{\prime \prime} \leq 14$ is given in [12]. From that chart we can see that

Table 4.3: Molecular constants ( $\mathrm{cm}^{-1}$ ) for the ${ }^{1} \Sigma_{0+u}$ state

| State | Mol. Const. | ${ }^{(79,99)} \cdot \mathrm{Br}_{2}$ | ${ }^{(81,81)} \mathrm{Br}_{2}$ | ${ }^{(79,81)} \mathrm{Br}_{2}$ |
| :---: | :--- | :--- | :--- | ---: |
| ${ }^{1} \Sigma_{0+}{ }^{+}{ }_{u}$ | $\omega_{e}$ | 325.3213 | 321.29 | 323.3056 |
| $v^{\prime \prime} \leq 10$ | $\omega_{e} x_{e}$ | 1.07742 | 1.064 | 1.0707 |
| $v^{\prime}$ | $10^{3} \omega_{e} y_{e}$ | -2.29798 | -2.2134 | -2.2556 |
| $v^{\prime \prime}=1$ | $10^{2} B_{v}$ | 8.1627 | 7.9618 | 8.0622 |
|  | $10^{8} D_{v}$ | 2.108 | 2.005 | 2.011 |
|  | $-10^{13} H_{v}$ | 2.89 | 0.0 | 1.445 |
| $v^{\prime \prime}=2$ | $10^{2} B_{v}$ | 8.1304 | 7.9306 | 8.0305 |
|  | $10^{8} D_{v}$ | 2.116 | 2.013 | 2.0645 |
|  | $-10^{13} H_{v}$ | 2.88 | 0.0 | 1.44 |

Table 4.4: A part of the particle densities (in $\mathrm{cm}^{-3}$ ) on $v^{\prime \prime}=1,{ }^{(79,79)} \mathrm{Br}_{2}$

| $v^{n}$ | $P, R(J=$ even $)$ | Density | $P, R(J=$ odd $)$ | Density |
| :--- | :--- | :---: | :--- | :---: |
| 1 | 0 | $1.4624 \times 10^{12}$ | 1 | $7.3060 \times 10^{12}$ |
| 1 | 2 | $7.2945 \times 1012$ | 3 | $1.6980 \times 10^{13}$ |
| 1 | 4 | $1.3058 \times 10^{13}$ | 5 | $2.6494 \times 10^{13}$ |
| 1 | 6 | $1.8698 \times 10^{13}$ | 7 | $3.5758 \times 10^{13}$ |
| 1 | 8 | $2.4162 \times 10^{13}$ | 9 | $4.689 \times 10^{13}$ |
| 1 | 10 | $2.9402 \times 10^{13}$ | 11 | $5.3206 \times 10^{13}$ |
| 1 | 12 | $3.4372 \times 10^{13}$ | 13 | $6.1237 \times 10^{13}$ |
| 1 | 14 | $3.9029 \times 10^{13}$ | 15 | $6.8715 \times 10^{13}$ |
| 1 | 16 | $4.3337 \times 10^{13}$ | 17 | $7.5583 \times 10^{13}$ |
| 1 | 18 | $4.7264 \times 10^{13}$ | 19 | $8.1793 \times 10^{13}$ |
| 1 | 20 | $5.0783 \times 10^{13}$ | 21 | $8.7305 \times 10^{13}$ |
| 1 | 22 | $5.3874 \times 10^{13}$ | 23 | $9.2091 \times 10^{13}$ |
| 1 | 24 | $5.6523 \times 10^{13}$ | 25 | $9.6132 \times 10^{13}$ |
| 1 | 26 | $5.8721 \times 10^{13}$ | 27 | $9.9417 \times 10^{13}$ |
| 1 | 28 | $6.0466 \times 10^{13}$ | 29 | $1.0195 \times 10^{14}$ |
| 1 | 30 | $6.1761 \times 10^{13}$ | 31 | $1.0374 \times 10^{14}$ |
| 1 | 32 | $6.2614 \times 10^{13}$ | 33 | $1.0480 \times 10^{14}$ |
| 1 | 34 | $6.3039 \times 10^{13}$ | 35 | $1.0516 \times 10^{14}$ |
| 1 | 36 | $6.3054 \times 10^{13}$ | 37 | $1.0486 \times 10^{14}$ |
| 1 | 38 | $6.2681 \times 10^{13}$ | 39 | $1.0393 \times 10^{14}$ |
| 1 | 40 | $6.1947 \times 10^{13}$ | 41 | $1.0242 \times 10^{14}$ |

transitions $17^{\prime}-2^{\prime \prime}$ should be very strong. Transitions $14^{\prime}-1^{\prime \prime}, 23^{\prime}-3^{\prime \prime}$ will be strong but not as strong as the $17^{\prime}-2^{\prime \prime}$ transition. The Franck-Condon factors used for our calculation are listed in appendix $B$.

The distribution of bromine isotopes also affects the transition intensity. Since the ${ }^{(79,81)} B r_{2}$ are twice as numerous as ${ }^{(79,79)} B r_{2}$ and ${ }^{(81,81)} B r_{2},{ }^{(79,81)} B r_{2}$ transitions will have intensities twice as big as similar transitions in ${ }^{(79,79)} \mathrm{Br}_{2}$ and ${ }^{(81,81)} \mathrm{Br}_{2}$.

### 4.4 Calculating the integrated absorption coefficient

From Eqn (2.63) we knew that we have to obtain the integrated absorption coefficient $\int k_{\nu} d \nu$ in order to obtain the experimental measure of the total strength of an electronic transition. We used several steps to obtain the integrated area, $\int k_{\nu} d \nu$.

First, the coordinates of the lower left and upper right corners of each $B r_{2}$ absorption line were calaulated and fixed. Then we used a digitizer to obtain a set of data, $x$ and y coordinates. The abscissa x represented $\nu$ in $\mathrm{cm}^{-1}$ and the ordinate y represented the intensity $I_{\nu}$. The program VDIGIT (provided by the Computing Center at UBC) run from a VICTOR9000 terminal was used to create data files. Moving the cursor along the absorption line one can obtained a set of data, i.e. a set of $\nu$ and $I_{\nu}$ values. Since the input intensity $I_{0}$ varies with time, a line between A and B was choosen to represent an approximate $I_{0}$ (see figure 4.7).

If several absorption lines overlap each other (see figure 4.8), we digitized them together.

Second, one can obtain a series of $k_{\nu}$ values by using Eqn.(2.46), and then one can obtain a set of $\nu$ and $k_{\nu}$ values for each absorption line. By using those $\nu$ and $k_{\nu}$ values one can obtain the values of $\int k_{\nu} d \nu$ using a computer.

Third, some apparently single lines were checked to see if they were, in fact, overlapped


Figure 4.7: Digitizing an absorption line
or not. We used two different methods to get two areas, using trapezoidal rule to get area $A_{1}$ and assuming $k_{\nu}$ as a Gaussian distrubution to get area $A_{2}$. Then we compared the two areas. If the area $A_{2}$ was same as the area $A_{1}\left(A_{2}\right.$ may be somewhat larger than $A_{1}$ because the Gaussian distrubution has long wings which may have been neglected by the first method), the line was not overlapped. If the area $A_{2}$ was much larger than $A_{1}$, the line was overlapped.

We also checked the half width, $\Delta \nu$, for each absorption line. If the line is overlapped, the measured half width will be wider than the Gaussian width. At the half-height of the band, we have

$$
\begin{equation*}
k_{\frac{1}{2}}=\frac{k_{\max }-k_{\min }}{2}=-\frac{1}{2 L} \ln \frac{I_{\min }}{I_{0}} \tag{4.78}
\end{equation*}
$$

From Fig. 2.4 we can find


Figure 4.8: Overlapped absorption lines

$$
\begin{equation*}
\Delta \nu=\nu_{2}-\nu_{1} \tag{4.79}
\end{equation*}
$$

Independently measurements of $\int k_{\nu} d \nu$ agreed to within $\pm 3.0 \%$ except for the weakest lines where the difference approached $\pm 6.0 \%$.

## Chapter 5

## The Results and Discussions

After analysing the spectrum, we obtained data for the following bands:

$$
\begin{array}{ccc}
14^{\prime}-1^{\prime \prime} & { }_{(79,79)}^{(79} r_{2} & 1 \leq J^{\prime \prime} \leq 19 \\
15^{\prime}-1^{\prime \prime} & (79,79) B r_{2} & 57 \leq J^{\prime \prime} \leq 63 \\
17^{\prime}-2^{\prime \prime} & (79,79) B r_{2} & 0 \leq J^{\prime \prime} \leq 21 \\
18^{\prime}-2^{\prime \prime} & { }_{(79,79)}^{(79} r_{2} & 53 \leq J^{\prime \prime} \leq 59 \\
19^{\prime}-2^{\prime \prime} & (79,79) B r_{2} & 74 \leq J^{\prime \prime} \leq 78 \\
14^{\prime}-1^{\prime \prime} & (79,81) B r_{2} & 1 \leq J^{\prime \prime} \leq 11 \\
15^{\prime}-1^{\prime \prime} & (79,81) B r_{2} & 55 \leq J^{\prime \prime} \leq 61 \\
17^{\prime}-2^{\prime \prime} & (79,81) B r_{2} & 0 \leq J^{\prime \prime} \leq 16 \\
18^{\prime}-2^{\prime \prime} & { }_{(79,81)}^{\left(7 r_{2}\right.} \quad 51 \leq J^{\prime \prime} \leq 57 \\
19^{\prime}-2^{\prime \prime} & (79,81) B r_{2} & 73 \leq J^{\prime \prime} \leq 78 \\
15^{\prime}-1^{\prime \prime} & (81,81) B r_{2} & 53 \leq J^{\prime \prime} \leq 60 \\
17^{\prime}-2^{\prime \prime} & (81,81) B r_{2} & 0 \leq J^{\prime \prime} \leq 8 \\
18^{\prime}-2^{\prime \prime} & (81,81) B r_{2} & 50 \leq J^{\prime \prime} \leq 56
\end{array}
$$

By using Eqn.(2.63) we estimated values for the electronic transition probability $\left.\mathbf{R}_{\mathbf{e}}\right|^{\mathbf{2}}$ for each band. Here we give a detailed sample calculation that shows how one goes from $\int k_{\nu} d \nu$ to $\left|R_{e}\right|^{2}$ with all factors explicitly given.

From Eqn.(2.63), one can obtain Eqn.(5.80):

$$
\begin{equation*}
\left|R_{e}\right|^{2}=\frac{\int k_{\nu} d \nu}{N_{m v^{\prime \prime} J^{\prime \prime}} \nu_{n m, v^{\prime \prime} J^{\prime \prime}}\left(\frac{8 \pi^{3}}{3 h c}\right)\left|R_{v i b .}^{v^{\prime} v^{\prime \prime}}\right|^{2} \frac{\sum_{M^{\prime} M^{\prime \prime}} \mid R_{\text {rot.t. }}^{\left.J^{\prime \prime}\right|^{\prime \prime}}}{2 J^{\prime \prime}+1}} \tag{5.80}
\end{equation*}
$$

For $\mathrm{P}(11)$ of band $14^{\prime}-1^{\prime \prime}$ of ${ }^{(79,79)} B r_{2}$, the $\left|R_{e}\right|^{2}$ value is given by

$$
\begin{align*}
\left|R_{e}\right|^{2} & =\frac{2.3694 \times 10^{-4}}{5.3206 \times 10^{13} \cdot 17469.499 \cdot\left(4.1623 \times 10^{17}\right) \cdot 0.00509 \cdot \frac{11}{23}} \\
& =2.52 \times 10^{-37}\left(\mathrm{erg} \cdot \mathrm{~cm}^{3}\right) \tag{5.81}
\end{align*}
$$

For the overlapped lines, a $\int k_{\nu} d \nu$ over the total area has been used. For example, the overlap of the three lines, $\mathrm{P}(54): 18^{\prime}-2^{\prime \prime}$ of ${ }^{(79,79)} B r_{2} ; \mathrm{R}(8): 14^{\prime}-1^{\prime \prime}$ of ${ }^{(79,79)} B r_{2}$ and $R(77): 19^{\prime}-2^{\prime \prime}$ of ${ }^{(79,79)} B r_{2}$, Eqn.(5.80) can be written as:

$$
\begin{equation*}
\left|R_{e}\right|^{2}=\frac{\int k_{\nu_{1}} d \nu+\int k_{\nu_{2}} d \nu+\int k_{\nu_{3}} d \nu}{C_{1}+C_{2}+C_{3}} \tag{5.82}
\end{equation*}
$$

where $C_{1}, C_{2}$ and $C_{3}$ are the denominators in Eqn.(5.80) for $\mathrm{P}(54), \mathrm{R}(8)$ and $\mathrm{R}(77)$, respectively.

The results of $\left|R_{e}\right|^{2}$ for the band $14^{\prime}-1^{\prime \prime}$ of ${ }^{(79,79)} B r_{2}$ is shown in table 5.5. The results for all other measured lines are showed in appendix D.

Taking the average of all values of $\left|\mathbf{R}_{\mathbf{e}}\right|^{\mathbf{2}}$ from table 5.5 we obtained Eqn.(5.83), the average value and standard diviation of the electronic transition probability.

$$
\begin{equation*}
\left|R_{e}\right|^{2}=(2.54 \pm 0.28) \times 10^{-37}\left(\mathrm{erg} \cdot \mathrm{~cm}^{3}\right) \tag{5.83}
\end{equation*}
$$

Because we only obtained the small part of spectrum of molecular bromine from our experiment, some of the lines in the spectrum were overlapped with some other lines which cannot be identified. So, for those lines we cannot obtain better values of $\left|\mathbf{R}_{\mathbf{e}}\right|^{\mathbf{2}}$ in the band. Therefore when we calculate the values of $\left|\mathbf{R e}_{\mathbf{e}}\right|^{2}$, we did not take into

Table 5.5: $\left|\mathbf{R}_{\mathrm{e}}\right|^{2}$ values for $14^{\prime}-1^{\prime \prime}$ of ${ }^{(79,79)} B r_{2}$

| $\mathrm{P}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|\mathbf{R}_{\mathrm{e}}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)$ | 17474.510 | $7.3066 \times 10^{12}$ | $2.3747 \times 10^{-4}$ | $2.82 \times 10^{-37}$ | $2.30 \times 10^{-2}$ |
| $\mathrm{P}(4)$ | 17473.655 | $1.3058 \times 10^{13}$ | $3.8263 \times 10^{-4}$ | $2.11 \times 10^{-37}$ | $2.07 \times 10^{-2}$ |
| $\mathrm{P}(6)$ | 17472.770 | $1.8698 \times 10^{13}$ | $0.7201 \times 10^{-4}$ | $2.25 \times 10^{-37}$ | $1.46 \times 10^{-2}$ |
| $\mathrm{P}(7)$ | 17472.237 | $3.5758 \times 10^{13}$ | $1.8767 \times 10^{-4}$ | $2.85 \times 10^{-37}$ | $2.01 \times 10^{-2}$ |
| $\mathrm{P}(8)$ | 17471.645 | $2.4162 \times 10^{13}$ | $1.0942 \times 10^{-4}$ | $2.60 \times 10^{-37}$ | $2.25 \times 10^{-2}$ |
| $\mathrm{P}(9)$ | 17470.987 | $4.4689 \times 10^{13}$ | $1.8651 \times 10^{-4}$ | $2.37 \times 10^{-37}$ | $2.27 \times 10^{-2}$ |
| $\mathrm{P}(11)$ | 17469.499 | $5.3206 \times 10^{13}$ | $2.3694 \times 10^{-4}$ | $2.52 \times 10^{-37}$ | $2.12 \times 10^{-2}$ |
| $\mathrm{P}(12)$ | 17468.656 | $3.4372 \times 10^{13}$ | $1.5725 \times 10^{-4}$ | $2.58 \times 10^{-37}$ | $2.17 \times 10^{-2}$ |
| $\mathrm{P}(13)$ | 17467.756 | $6.1237 \times 10^{14}$ | $1.5741 \times 10^{-4}$ | $2.27 \times 10^{-37}$ | $2.07 \times 10^{-2}$ |
| $\mathrm{P}(14)$ | 17466.796 | $3.9029 \times 10^{13}$ | $3.0943 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.39 \times 10^{-2}$ |
| $\mathrm{P}(15)$ | 17465.771 | $6.8715 \times 10^{13}$ | $4.5367 \times 10^{-4}$ | $2.06 \times 10^{-37}$ | $2.47 \times 10^{-2}$ |
| $\mathrm{P}(16)$ | 17464.684 | $4.3337 \times 10^{13}$ | $1.9524 \times 10^{-4}$ | $2.51 \times 10^{-37}$ | $2.05 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} \mathrm{J}^{\prime \prime}}$ | $\int k_{\nu} d \nu m^{-2}$ | $\mid \mathbf{R}_{\mathrm{e}} \mathrm{l}^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(4)$ | 17474.546 | $1.3058 \times 10^{13}$ | $10.4649 \times 10^{-4}$ | $2.82 \times 10^{-37}$ | $2.78 \times 10^{-2}$ |
| $\mathrm{R}(5)$ | 17474.359 | $2.6494 \times 10^{13}$ | $1.5968 \times 10^{-4}$ | $2.98 \times 10^{-37}$ | $2.21 \times 10^{-2}$ |
| $\mathrm{R}(7)$ | 17473.761 | $3.5758 \times 10^{13}$ | $2.5813 \times 10^{-4}$ | $2.12 \times 10^{-37}$ | $1.94 \times 10^{-2}$ |
| $\mathrm{R}(8)$ | 17473.368 | $2.4162 \times 10^{13}$ | $1.5832 \times 10^{-4}$ | $3.00 \times 10^{-37}$ | $2.18 \times 10^{-2}$ |
| $\mathrm{R}(9)$ | 17472.926 | $4.4689 \times 10^{13}$ | $3.8333 \times 10^{-4}$ | $2.38 \times 10^{-37}$ | $2.17 \times 10^{-2}$ |
| $\mathrm{R}(11)$ | 17471.841 | $5.3206 \times 10^{13}$ | $2.3285 \times 10^{-4}$ | $2.27 \times 10^{-37}$ | $1.94 \times 10^{-2}$ |
| $\mathrm{R}(12)$ | 17471.199 | $3.4372 \times 10^{13}$ | $1.6754 \times 10^{-4}$ | $2.53 \times 10^{-37}$ | $2.42 \times 10^{-2}$ |
| $\mathrm{R}(13)$ | 17470.501 | $6.1237 \times 10^{14}$ | $2.6743 \times 10^{-4}$ | $2.28 \times 10^{-37}$ | $1.96 \times 10^{-2}$ |
| $\mathrm{R}(14)$ | 17469.749 | $3.9029 \times 10^{13}$ | $1.4127 \times 10^{-4}$ | $2.22 \times 10^{-37}$ | $1.88 \times 10^{-2}$ |
| $\mathrm{R}(15)$ | 17468.925 | $6.8715 \times 10^{14}$ | $3.0055 \times 10^{-4}$ | $2.78 \times 10^{-37}$ | $2.03 \times 10^{-2}$ |
| $\mathrm{R}(16)$ | 17468.042 | $4.3337 \times 10^{13}$ | $2.7618 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.53 \times 10^{-2}$ |
| $\mathrm{R}(17)$ | 17467.095 | $7.5583 \times 10^{14}$ | $3.6602 \times 10^{-4}$ | $2.54 \times 10^{-37}$ | $2.09 \times 10^{-2}$ |
| $\mathrm{R}(18)$ | 17466.096 | $4.7264 \times 10^{13}$ | $7.0570 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.25 \times 10^{-2}$ |
| $\mathrm{R}(19)$ | 17465.032 | $8.1793 \times 10^{14}$ | $4.6456 \times 10^{-4}$ | $2.29 \times 10^{-37}$ | $2.46 \times 10^{-2}$ |

Table 5.6: $\left|R_{e}\right|^{2}$ value for overlapped lines

| $\mathrm{P}, \mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m \mathrm{~m}^{\prime \prime} \mathrm{J}^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|\mathbf{R}_{\mathrm{e}}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(2)$ | 17474.273 | $7.2945 \times 10^{12}$ | $1.0087 \times 10^{-4}$ | $9.34 \times 10^{-37}$ | $2.36 \times 10^{-2}$ |
| $\mathrm{P}(3)$ | 17473.990 | $1.6980 \times 10^{13}$ | $1.0253 \times 10^{-4}$ | $3.81 \times 10^{-37}$ | $2.58 \times 10^{-2}$ |
| $\mathrm{P}(5)$ | 17473.234 | $2.6494 \times 10^{13}$ | $1.7751 \times 10^{-4}$ | $3.98 \times 10^{-37}$ | $2.80 \times 10^{-2}$ |
| $\mathrm{P}(10)$ | 17470.271 | $2.9402 \times 10^{13}$ | $2.9105 \times 10^{-4}$ | $5.62 \times 10^{-37}$ | $0.83 \times 10^{-2}$ |
| $\mathrm{R}(6)$ | 17444.090 | $1.8689 \times 10^{14}$ | $1.2210 \times 10^{-4}$ | $3.28 \times 10^{-37}$ | $2.47 \times 10^{-72}$ |
| $\mathrm{R}(10)$ | 17472.412 | $2.9402 \times 10^{13}$ | $2.4368 \times 10^{-4}$ | $4.27 \times 10^{-37}$ | $2.09 \times 10^{-2}$ |

account those lines, for instance, in band $14^{\prime}-1^{\prime \prime}$ of ${ }^{(79,79)} B r_{2}$, the value of $\left|\mathbf{R}_{\mathbf{e}}\right|^{2}$ of those lines overlapped with the line cannot be identified are showed in table 5.6.

After calculating the electronic transition probability for all bands which we have analysed, we obtained the table 5.7. The mean value of $\left|\mathbf{R}_{\mathbf{e}}\right|^{2}$ is $(2.52 \pm 0.25) \times$ $10^{-37}\left(\mathrm{erg} \cdot \mathrm{cm}^{3}\right)$

The average radiative lifetime, $\tau_{\text {rad }}$, for each vibrational state $v^{\prime}$ was obtained by using Eqn.(2.67) and the results are summarized in table $5: 8$ for the region $17464 \mathrm{~cm}^{-1}$ to $17480 \mathrm{~cm}^{-1}$. In the ground electronic state there are around 137 vibrational levels $v^{\prime \prime}$. F.C.F. were only available to evaluate $\Sigma q_{v^{\prime} v^{\prime \prime}} \nu^{3}$ up to $v^{\prime \prime}=10$ for $v^{\prime}=14,15,17,18,19$ for ${ }^{(79,79)} B r_{2}$ and ${ }^{(81,81)} B r_{2} ; v^{\prime \prime}=20$ for $v^{\prime}=14,15,17 ; v^{\prime \prime}=12$ for $v^{\prime}=18,19$ for ${ }^{(79,81)} B r_{2}$ (see appendix E). The frequency of each observed line was used during the calculation of $\tau_{\text {rad }}$.

The results of radiative lifetime measurements obtained by Clyne [8] are showed in table 5.9 where the calculated $\tau_{\text {rad. }}$ values are based on Le Roy's work [24].

Le Roy used radial wavefunction to calculate diatomic molecule absorption coefficients. In Clyne's work, $\tau_{\text {rad. }}$. were obtained from measurements of collision-free lifetimes $\tau_{0}$ of $B r_{2}(\mathrm{~B})$ excited molecules. The collision-free lifetime is given by Eqn.(5.84).

Table 5.7: Mean $\left|\mathbf{R}_{\mathbf{e}}\right|^{\mathbf{2}}$ for all identified bands

| Band | Average $\left\|R_{e}\right\|^{2}$ | Standard diviation | Error |
| :---: | :---: | :---: | :---: |
| $\left(14^{\prime}-1^{\prime \prime}\right)^{79-79}$ | $2.54 \times 10^{-37}$ | $0.28 \times 10^{-37}$ | 11\% |
| $\left(15^{\prime}-1^{\prime \prime}\right)^{79-79}$ | $2.43 \times 10^{-37}$ | $0.18 \times 10^{-37}$ | 7\% |
| $\left(17^{\prime}-2^{\prime \prime}\right)^{79-79}$ | $2.58 \times 10^{-37}$ | $0.24 \times 10^{-37}$ | 9\% |
| $\left(18^{\prime}-2^{\prime \prime}\right)^{79-79}$ | $2.62 \times 10^{-37}$ | $0.25 \times 10^{-37}$. | 10\% |
| $\left(19^{\prime}-2^{\prime \prime}\right)^{79-79}$ | $2.66 \times 10^{-37}$ | $0.27 \times 10^{-37}$ | 10\% |
| $\left(14^{\prime}-1^{\prime \prime}\right)^{79-81}$ | $2.67 \times 10^{-37}$ | $0.23 \times 10^{-37}$ | 9\% |
| $\left(15^{\prime}-1^{\prime \prime}\right)^{79-81}$ | $2.45 \times 10^{-37}$ | $0.21 \times 10^{-37}$ | $9 \%$ |
| $\left(17^{\prime}-2^{\prime \prime}\right)^{79-81}$ | $2.58 \times 10^{-37}$ | $0.20 \times 10^{-37}$ | $8 \%$ |
| $\left(18^{\prime}-2^{\prime \prime}\right)^{79-81}$ | $2.48 \times 10^{-37}$ | $0.27 \times 10^{-37}$ | 11\% |
| $\left(19^{\prime}-2^{\prime \prime}\right)^{79-81}$ | $2.47 \times 10^{-37}$ | $0.27 \times 10^{-37}$ | 11\% |
| $\left(15^{\prime}-1^{\prime \prime}\right)^{81-81}$ | $2.40 \times 10^{-37}$ | $0.24 \times 10^{-37}$ | 10\% |
| $\left(17^{\prime}-2^{\prime \prime}\right)^{81-81}$ | $2.47 \times 10^{-37}$ | $0.32 \times 10^{-37}$. | 13\% |
| $\left(18^{\prime}-2^{\prime \prime}\right)^{81-81}$ | $2.47 \times 10^{-37}$ | $0.31 \times 10^{-37}$ | 13\% |

Table 5.8: $\tau_{\text {rad. }}$ for the excited state $v^{\prime}$

| Isotope $B r_{2}$ | Excited state $v^{\prime}$ | Average $\tau_{\text {rad. }}$ | Error |
| :--- | :--- | :--- | :--- |
| $B r_{2}(79-79)$ | 14 | $17.1 \mu \mathrm{~s}$ | $1.9 \mu \mathrm{~s}$ |
| $B r_{2}(79-81)$ | 14 | $9.8 \mu \mathrm{~s}$ | $1.1 \mu \mathrm{~s}$ |
| $B r_{2}(79-79)$ | 17 | $22.2 \mu \mathrm{~s}$ | $2.4 \mu \mathrm{~s}$ |
| $B r_{2}(79-81)$ | 17 | $17.5 \mu \mathrm{~s}$ | $1.9 \mu \mathrm{~s}$ |
| $B r_{2}(81-81)$ | 17 | $23.6 \mu \mathrm{~s}$ | $2.6 \mu \mathrm{~s}$ |
| $B r_{2}(79-79)$ | 18 | $24.3 \mu \mathrm{~s}$ | $2.7 \mu \mathrm{~s}$ |
| $B r_{2}(79,81)$ | 18 | $22.0 \mu \mathrm{~s}$ | $2.4 \mu \mathrm{~s}$ |
| $B r_{2}(81-81)$ | 18 | $24.5 \mu \mathrm{~s}$ | $2.7 \mu \mathrm{~s}$ |
| $B r_{2}(79-79)$ | 19 | $24.5 \mu \mathrm{~s}$ | $2.7 \mu \mathrm{~s}$ |
| $B r_{2}(79-81)$ | 19 | $23.4 \mu \mathrm{~s}$ | $2.6 \mu \mathrm{~s}$ |
| $B r_{2}(79-99)$ | 15 | $18.0 \mu \mathrm{~s}$ | $2.0 \mu \mathrm{~s}$ |
| $B r_{2}(79-81)$ | 15 | $11.0 \mu \mathrm{~s}$ | $1.2 \mu \mathrm{~s}$ |
| $B r_{2}(81-81)$ | 15 | $18.4 \mu \mathrm{~s}$ | $2.0 \mu \mathrm{~s}$ |

Table 5.9: The $\tau_{\text {rad }}$ of ${ }^{(79,79)} B r_{2}$ obtained by Clyen

| $v^{\prime}$ | Mean $\left\|R_{e}\right\|^{2}$ | $\tau_{\text {rad. }} \mu \mathrm{s}$ (cal.) | $\tau_{\text {rad. }} \mu \mathrm{s}$ (obs.) | Error |
| :---: | :--- | :--- | :--- | ---: |
| 11 | $2.04 \times 10^{-37}$ | 15.8 | 5.1 | +1.5 |
|  |  |  | 7.4 | -0.9 |
| 14 | $1.97 \times 10^{-37}$ | 15.9 | 11.3 | +1.5 |
|  |  |  |  | -1.0 |
| 19 | $1.87 \times 10^{-37}$ | 20.8 | 6.1 | +2.0 |
|  |  |  |  | +2.5 |
| 20 | $1.85 \times 10^{-37}$ | 21.9 |  | -1.9 |

$$
\begin{equation*}
\frac{1}{\tau_{0}}=\frac{1}{\tau_{\text {rad }}}+k_{v^{\prime}} J^{\prime}\left(J^{\prime}+1\right) \tag{5.84}
\end{equation*}
$$

where $k_{v^{\prime}}$ is a constant dependent on $v^{\prime}$. For such a case, a plot of $\frac{1}{\tau_{0}}$ vs. $J^{\prime}\left(J^{\prime}+1\right)$ has been given and the intercept equal to $\frac{1}{\tau_{\text {rad }}}$. From table 5.9 one can note that the calculated values are two to three times larger than the observed one, while our results (see table 5.8) are closer to Le Roy's estimates.

The values of $\tau_{\text {rad: }}$ are very sensitive to the values of $\Sigma q_{v^{\prime} v^{\prime \prime}} \nu^{3}$ used in Eqn.(2.67). As more terms are added to the sum, the smaller $\tau_{\text {rad }}$ becomes. Table 5.10 shows the difference among the values of $\Sigma q_{v^{\prime} v^{\prime \prime}} \nu^{3}$ as more terms are added for the case of the $17^{\prime}-2^{\prime \prime}$ band of ${ }^{(79,81)} B r_{2}$. If we can obtain all the F.C.F. and sum over them, the value of $\Sigma q_{v^{\prime} v^{\prime \prime}}$ shoud equal to 1 and then Eqn.(2.67) approximately can be written as Eqn.(5.85).

$$
\begin{equation*}
\tau_{\text {rad. }}=\frac{3 h}{64 \pi^{4}\left|\mathbf{R}_{\mathrm{e}}\right|^{2} \nu^{3}} \tag{5.85}
\end{equation*}
$$

the radiative lifetime $\tau_{\text {rad. }}$ has been given in table 5.11 by using Eqn.(5.85).

Table 5.10: The values of $\Sigma q_{v^{\prime} v^{\prime \prime}} \nu^{3}$

| Terms of F.C.F. | $\Sigma q_{v^{\prime} v^{\prime \prime}} \nu^{3}$ | Terms of F.C.F. | $\Sigma q_{v^{\prime} v^{\prime \prime}} \nu^{3}$ |
| :--- | :---: | :--- | :---: |
| 3 | $18.707 \times 10^{10}$ | 13 | $58.959 \times 10^{10}$ |
| 4 | $32.259 \times 10^{10}$ | 14 | $62.480 \times 10^{10}$ |
| 5 | $36.552 \times 10^{10}$ | 15 | $62.625 \times 10^{10}$ |
| 6 | $36.873 \times 10^{10}$ | 16 | $64.518 \times 10^{10}$ |
| 7 | $43.126 \times 10^{10}$ | 17 | $67.299 \times 10^{10}$ |
| 8 | $48.417 \times 10^{10}$ | 18 | $67.395 \times 10^{10}$ |
| 9 | $48.466 \times 10^{10}$ | 19 | $68.991 \times 10^{10}$ |
| 10 | $51.961 \times 10^{10}$ | 20 | $71.198 \times 10^{10}$ |
| 11 | $56.377 \times 10^{10}$ | 21 | $71.248 \times 10^{10}$ |

However, now there is a difficulty in choosing a suitable value for $\nu$. We used the frequency of each observed line to calculate $\Sigma q_{v^{\prime}} v^{\prime \prime} \nu^{3}$. One can chose the frequency which corresponds to the strongest F.C.F.

Based on Le Roy's study, Clyne obtained the values of $\left|R_{e}\right|^{2}$ from Eqn.(5.86).

$$
\begin{equation*}
\left|R_{e}\right|^{2}=[0.3905+0.265(r-2.3)]^{2} \tag{5.86}
\end{equation*}
$$

the mean $\left|R_{e}\right|^{2}$ were given in table 5.9. From table 5.8 one can also see that the electronic transition probability, $\left|R_{e}\right|^{2}$, are in close agreement with Clyne's work.
. In order to see the spontaneous predissociation rate, $\Gamma_{P}$, of $B r_{2} B^{3} \Pi_{o+u}$ state one can draw a graph $\frac{1}{I_{F}}$ vs. $J^{\prime}\left(J^{\prime}+1\right)$. The graphs shown in figure 5.9 does not follow Eqn.(2.70). From reference [25], we can obtain figure 5.10 (by using their data). In contract, one can obtain the firgure 5.11 from our data using the same method.

Comparing figure 5.10 and figure 5.11 one can see that they both have very similar shape. Figure 5.11 suggests that there is probably a predissociation in $v^{\prime}=14$ level near $J^{\prime}\left(J^{\prime}+1\right)$. This method cannot be used for $v^{\prime}=15,17,18,19$ levels because most of


Figure 5.9: + and $\Delta$ represent $P$ and $R$ branches

Table 5.11: $\tau_{\text {rad. }}$ for the excited state $v^{\prime}$

| Isotope | Excited state $v^{\prime}$ | Average $\tau_{\text {rad }}$ | Error |
| :---: | :--- | :--- | :--- |
| $B r_{2}(79-79)$ | 14 | $2.5 \mu \mathrm{~s}$ | $0.3 \mu \mathrm{~s}$ |
| $B r_{2}(79-81)$ | 14 | $2.7 \mu \mathrm{~s}$ | $0.2 \mu \mathrm{~s}$ |
| $B r_{2}(79-79)$ | 17 | $2.6 \mu \mathrm{~s}$ | $0.2 \mu \mathrm{~s}$ |
| $B r_{2}(79-81)$ | 17 | $2.6 \mu \mathrm{~s}$ | $0.2 \mu \mathrm{~s}$ |
| $B r_{2}(81-81)$ | 17 | $2.5 \mu \mathrm{~s}$ | $0.3 \mu \mathrm{~s}$ |
| $B r_{2}(79-79)$ | 18 | $2.6 \mu \mathrm{~s}$ | $0.3 \mu \mathrm{~s}$ |
| $B r_{2}(79,81)$ | 18 | $2.5 \mu \mathrm{~s}$ | $0.3 \mu \mathrm{~s}$ |
| $B r_{2}(81-81)$ | 18 | $2.5 \mu \mathrm{~s}$ | $0.3 \mu \mathrm{~s}$ |
| $B r_{2}(79-79)$ | 19 | $2.7 \mu \mathrm{~s}$ | $0.3 \mu \mathrm{~s}$ |
| $B r_{2}(79-81)$ | 19 | $2.5 \mu \mathrm{~s}$ | $0.3 \mu \mathrm{~s}$ |
| $B r_{2}(79-79)$ | 15 | $2.4 \mu \mathrm{~s}$ | $0.2 \mu \mathrm{~s}$ |
| $B r_{2}(79-81)$ | 15 | $2.5 \mu \mathrm{~s}$ | $0.2 \mu \mathrm{~s}$ |
| $B r_{2}(81-81)$ | 15 | $2.4 \mu \mathrm{~s}$ | $0.2 \mu \mathrm{~s}$ |



Figure 5.10: $v^{\prime}=16, B^{3} \Pi_{o}+{ }_{u}$ state of ${ }^{(79,79)} B r_{2}$


Figure 5.11: $v^{\prime}=14, B^{3} \Pi_{o+u}$ state of ${ }^{(79,79)} B r_{2}$
lines from those $v^{\prime}$ states are overlapped. Therefore it is hard to determine if there is a predissociation or not for those vibrational states.

In this thesis, we have presented a detailed research of radiative lifetime, $\tau_{\text {rad }}$, of ${ }^{(79,79)} B r_{2},{ }^{(79,81)} B r_{2}$ and ${ }^{(81,81)} B r_{2}$. The apparatus and methods used to obtain the spectra and construction of the sample cells are described. The absorption and fluorescence spectra of the molecule bromine corresponding to the transitions between the ground state, $X^{1} \Sigma_{0+g}$, and excited state, $B^{3} \Pi_{0+u}$, have been measured from approximately 17464 $\mathrm{cm}^{-1}$ to $17480 \mathrm{~cm}^{-1}$. The radiative lifetimes $\tau_{\text {rad. }}$ for $v^{\prime}=14,15,17,18,19$ of ${ }^{(79,79)} B r_{2}$, ${ }^{(79,81)} B r_{2}$ and ${ }^{(81,81)} B r_{2}$ have been calculated from the spectra. However, there is a difficulty to determine the predissociations for some levels because of limited data.

## Appendix A

## The derivation of the transition probabilities

From quantum mechanics, we have

$$
\begin{equation*}
\mathbf{R}=\int \psi^{\prime \prime} \mathbf{M} \psi^{\prime \prime} \mathbf{d} \tau \tag{A.87}
\end{equation*}
$$

where

$$
\begin{equation*}
d \tau=d \tau_{e} r^{2} \sin \theta d r d \theta d \phi \tag{A.88}
\end{equation*}
$$

and

$$
\begin{equation*}
M \doteq M_{e}+M_{n} \tag{A.89}
\end{equation*}
$$

$d \tau_{e}$ is the volume element in the configuration space of the electrons.
$\mathbf{M}$ is the electronic momnent.
$M_{e}$ and $M_{n}$ depend on electrons and nuclei, respectrly.
In the $z$ direction, we have

$$
\begin{equation*}
M_{z}=M \cos \theta=\left(M_{e}+M_{N}\right) \cos \theta \tag{A.90}
\end{equation*}
$$

The complete eigenfunction of a molecule, to a first order approximation, is

$$
\begin{equation*}
\psi=\psi_{e} \cdot \frac{1}{r} \psi_{v} \cdot \psi_{r} \tag{A.91}
\end{equation*}
$$

where

Appendix A. The derivation of the transition probabilities
$\psi_{e}$ the electron eigenfunction.
$\psi_{v}$ the eigenfunction of a non simple harmonic vibration.
$\psi_{\tau}$ the eigenfunction of a rigid rotor.

Thus,

$$
\begin{equation*}
R_{z}=\int \psi_{e^{\prime}}^{*} M_{e} \psi_{e^{\prime \prime}} d \tau_{e} \int \psi_{v^{\prime}}^{*} \psi_{v^{\prime \prime}} d r \int \sin \theta \cos \theta \psi_{r^{\prime}}^{*} \psi_{r^{\prime \prime}} d \theta d \varphi \tag{A.92}
\end{equation*}
$$

Where we have used

$$
\begin{equation*}
\int \psi_{e^{\prime}}^{*} \psi_{e^{\prime \prime}} d \tau_{e}=0 \tag{A.93}
\end{equation*}
$$

Considering three dimensions, we can obtain the total matrix element for the system

$$
\begin{equation*}
\mathbf{R}^{\mathrm{nm}}=\mathbf{R}_{\mathbf{e}}^{\mathrm{nm}} \mathbf{R}_{\mathrm{vib} .}^{\mathrm{v}^{\prime} \mathrm{v}^{\prime \prime}} \mathbf{R}_{\text {rot. }}^{\mathrm{J}^{\prime} \mathrm{J}^{\prime \prime}} \tag{A.94}
\end{equation*}
$$

The transition probability is proportional to $\left|\mathbf{R}^{\mathbf{n m}}\right|^{\mathbf{2}}$.

## Appendix B

## The vibrational and rotational transition probabilities

## B. 1 Vibrational transition probability

From Eqn.(A.89) one know that in the electronic transition the intensity of the vibrational spectrum band is proportional to $\left|\int \psi_{v^{\prime}}^{*} \psi_{v^{\prime \prime}} d r\right|^{2}$ (F.C.F.). Where $\psi_{v^{\prime}}$ and $\psi_{v^{\prime \prime}}$ belong to different electronic states, and they are not orthogonal. The integral $\int \psi_{v^{\prime}}^{*} \psi_{v^{\prime \prime}}$ is called overlap integral. The intensity of a vibrational band depends on the level of overlap between $\psi_{v^{\prime}}$ and $\psi_{v^{\prime \prime}}$. If we knew the electronic and vibrational wavefunctions, we can obtain the transition probability from. Eqn.(A.89).

For the $B^{3} \Pi_{o^{+} u^{-}} X^{1} \Sigma_{0^{+} g}$ system of $B r_{2}$, all the Franck-Condon factors in the $B^{3} \Pi_{o+u}$ state were obtained from several papers. [3,12]

## B. 2 Calculation of the rotational transition probabilty

First one can consider the $z$ direction,

$$
\begin{equation*}
\sum_{M^{\prime} M^{\prime \prime}}\left|\mathbf{R}_{\text {rot. }}^{\mathbf{J}^{\prime} \mathbf{j}^{\prime \prime}}\right|^{2}=\sum_{\mathbf{M}^{\prime} \mathbf{M}^{\prime \prime}}\left|\int \sin \theta \cos \theta \psi_{\mathbf{r}^{\prime}}^{*} \psi_{\mathbf{r}^{\prime \prime}}^{*} \mathbf{d} \theta \mathbf{d} \varphi\right|^{2} \tag{B.95}
\end{equation*}
$$

where

$$
\begin{equation*}
\psi_{\tau}^{J, M}=N_{r} P_{J}^{|M|}(\cos \theta) e^{i M \varphi} \tag{B.96}
\end{equation*}
$$

Thus

$$
\begin{align*}
& \int \sin \theta \cos \theta\left[N_{r^{\prime}} N_{r^{\prime \prime}} \int e^{i\left(M^{\prime}-M^{\prime \prime}\right)} d \varphi\right] P_{J^{\prime}}^{\left|M^{\prime}\right|}(\cos \theta) P_{J^{\prime \prime}}^{\left|M^{\prime \prime}\right|}(\cos \theta) d \theta \\
= & 2 \pi N_{r^{\prime}} N_{r^{\prime \prime}} \int_{-1}^{+1} P_{J^{\prime}}^{|M|}(x) x P_{J^{\prime \prime}}^{|M|}(x) d x \tag{B.97}
\end{align*}
$$

where we have used

$$
\begin{equation*}
\int e^{i\left(M^{\prime}-M^{\prime \prime}\right)} d \varphi=2 \pi \delta_{M^{\prime} M^{\prime \prime}} \tag{B.98}
\end{equation*}
$$

Using the formulas

$$
\begin{gather*}
z P_{\nu}^{\mu}(z)=\frac{1}{2 \nu+1}\left[(\nu-\mu+1) P_{\nu+1}^{\mu}(z)+(\nu+\mu) P_{\nu-1}^{\mu}(z)\right]  \tag{B.99}\\
\int_{-1}^{+1} P_{l^{m}}(\mu) P_{l^{\prime}}^{m}(\mu) \dot{d} \mu=\frac{2}{2 l+1} \frac{(l+m)}{(l-m)!} \delta_{l l^{\prime}}  \tag{B.100}\\
N_{r}=(-1)^{m} \sqrt{\frac{(2 J+1)(J-M)!}{4 \pi(J+M)!}} \tag{B.101}
\end{gather*}
$$

In this case,

$$
\begin{align*}
z & =x  \tag{B.102}\\
\nu & =\mu  \tag{B.103}\\
\mu & =M  \tag{B.104}\\
l & =J^{\prime}  \tag{B.105}\\
l^{\prime} & =J^{\prime \prime}  \tag{B.106}\\
m & =M \tag{B.107}
\end{align*}
$$

So, in z direction one can obtain the transition probability,

$$
\begin{align*}
& \sum_{M^{\prime} M^{\prime \prime}}\left|\mathbf{R}_{\text {rot. } \mathbf{J}^{\prime} \mathbf{J}^{\prime \prime}}\right|^{2} \\
= & \sum_{M^{\prime} M^{\prime \prime}} \left\lvert\, \frac{2 \pi(-1)^{2 m}}{2 J^{\prime \prime}+1} \sqrt{\frac{\left(2 J^{\prime}+1\right)\left(J^{\prime}-M\right)!}{4 \pi\left(J^{\prime}+M\right)!} \sqrt{\frac{\left(2 J^{\prime \prime}+1\right)\left(J^{\prime \prime}-M\right)!}{4 \pi\left(J^{\prime \prime}+M\right)!}}} \begin{array}{l}
{\left[\left(J^{\prime \prime}-M+1\right) \delta_{J^{\prime}, J^{\prime \prime}+1}+\left(J^{\prime \prime}+M\right) \delta_{J^{\prime}, J^{\prime \prime}}\right]}
\end{array}\right.
\end{align*}
$$

Finally, for the three dimensional system one obtains

$$
\begin{equation*}
\sum_{M^{\prime} M^{\prime \prime}}\left|\mathbf{R}_{\mathbf{r o t} .}^{\mathbf{J}^{\prime} \mathbf{J}^{\prime \prime}}\right|^{\mathbf{2}=\mathbf{J}^{\prime \prime}} \tag{B.109}
\end{equation*}
$$

for the P branch, and

$$
\begin{equation*}
\sum_{M^{\prime} M^{\prime \prime}}\left|\mathbf{R}_{\text {rot. }}^{\mathrm{J}^{\prime} \mathrm{J}^{\prime \prime}}\right|^{2}=\mathbf{J}^{\prime \prime}+\mathbf{1} \tag{B.110}
\end{equation*}
$$

for the R branch.
Therefore,

$$
\begin{equation*}
\frac{\sum_{M^{\prime} M^{\prime \prime}}\left|\mathbf{R}_{\text {rot. }}^{\mathrm{J}^{\prime} \mathbf{J}^{\prime \prime}}\right|^{2}}{2 \mathbf{J}^{\prime \prime}+\mathbf{1}}=1 \tag{B.111}
\end{equation*}
$$

## Appendix C

## The density of molecular bromine in a particular rovibronic state

The hyperfine partition factor is $\frac{10}{16}=\frac{5}{8}$ for an ortho state (odd J), and $\frac{6}{10}=\frac{3}{8}$ for a para state (even J).

The density of a para state of ${ }^{(79,79)} B r_{2}$, at room temperature, satisfies the following equation

$$
\begin{align*}
N_{v^{\prime \prime} J^{\prime \prime}}= & \left.\frac{N_{0}}{V} \times 0.2554 \times \frac{e^{-\beta E_{v^{\prime \prime}}}}{\sum_{v^{\prime \prime}} e^{-\beta E_{v^{\prime \prime}}} \times \frac{e^{-\beta E_{e}}}{\sum_{n} e^{-\beta E_{e}}}} \begin{array}{rl} 
& 3\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J}^{\prime \prime}} \\
& \times\left[\frac{\sum_{\text {oddJ }}\left(2 J^{\prime \prime}\right.}{}+1\right) e^{-\beta E_{J^{\prime \prime}}}+3 \sum_{\text {evenJ } J^{\prime \prime}}\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}}
\end{array}\right]
\end{align*}
$$

The equation above can be written as

$$
\begin{align*}
N_{v^{\prime \prime} J^{\prime \prime}}= & \frac{N_{0}}{V} \times 0.2554 \times \frac{e^{-\beta E_{v^{\prime \prime}}}}{\sum_{v^{\prime \prime}} e^{-\beta E_{v^{\prime \prime}}}} \\
& \times\left[\frac{3\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}}}{\left.3 \sum_{J^{\prime \prime}}\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}}+2 \times \frac{1}{2} \sum_{J^{\prime \prime}}\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}}\right]}\right. \tag{C.113}
\end{align*}
$$

Then we can obtain

$$
\begin{align*}
N_{v^{\prime \prime} J^{\prime \prime}}= & \frac{N_{0}}{V} \times 0.2554 \times \frac{e^{-\beta E_{v^{\prime \prime}}}}{\sum_{v^{\prime \prime}} e^{-\beta E_{v^{\prime \prime}}} \times} \\
& \frac{3}{4} \frac{\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}}}{\sum_{J^{\prime \prime}}\left(2 J^{\prime \prime}+1\right) e^{-\beta E_{J^{\prime \prime}}}} \tag{C.114}
\end{align*}
$$

where $E_{e}$ is equal to zero for the ground electronic state.
In the same way we can obtain Eqn.(2.41).

## Appendix D

Identified and unused lines of Band $14^{\prime}-1^{\prime \prime}$

Table D.12: Band $14^{\prime \prime}-1^{\prime \prime}$ bromine $(79,81)$

| $\mathrm{P}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu c m^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu c m^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(3)$ | 17466.705 | $2.6458 \times 10^{13}$ | $0.7206 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.35 \times 10^{-2}$ |
| $\mathrm{P}(4)$ | 17466.358 | $3.3911 \times 10^{13}$ | $1.5938 \times 10^{-4}$ | $2.88 \times 10^{-37}$ | $2.28 \times 10^{-2}$ |
| $\mathrm{P}(5)$ | 17465.965 | $4.1285 \times 10^{13}$ | $2.2497 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.22 \times 10^{-2}$ |
| $\mathrm{P}(6)$ | 17465.498 | $4.8563 \times 10^{13}$ | $2.5790 \times 10^{-4}$ | $2.42 \times 10^{-37}$ | $2.33 \times 10^{-2}$ |
| $\mathrm{P}(7)$ | 17464.969 | $5.5729 \times 10^{13}$ | $4.5523 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.66 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu c m^{-1}$ |
| $\mathrm{R}(3)$ | 17467.410 | $2.6458 \times 10^{13}$ | $1.2148 \times 10^{-4}$ | $2.29 \times 10^{-37}$ | $2.24 \times 10^{-2}$ |
| $\mathrm{R}(4)$ | 17467.268 | $3.3911 \times 10^{13}$ | $1.6490 \times 10^{-4}$ | $2.50 \times 10^{-37}$ | $2.12 \times 10^{-2}$ |
| $\mathrm{R}(5)$ | 17467.064 | $4.1285 \times 10^{13}$ | $1.7696 \times 10^{-4}$ | $2.24 \times 10^{-37}$ | $1.91 \times 10^{-2}$ |
| $\mathrm{R}(6)$ | 17466.796 | $4.8653 \times 10^{13}$ | $3.0943 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.54 \times 10^{-2}$ |
| $\mathrm{R}(7)$ | 17466.477 | $5.5729 \times 10^{13}$ | $2.9266 \times 10^{-4}$ | $2.88 \times 10^{-37}$ | $2.16 \times 10^{-2}$ |
| $\mathrm{R}(8)$ | 17466.096 | $6.2766 \times 10^{13}$ | $7.0570 \times 10^{-4}$ | $2.79 \times 10^{-37}$ | $2.35 \times 10^{-2}$ |
| $\mathrm{R}(9)$ | 17465.655 | $6.9659 \times 10^{13}$ | $5.8730 \times 10^{-4}$ | $2.70 \times 10^{-37}$ | $2.23 \times 10^{-2}$ |
| $\mathrm{R}(10)$ | 17465.152 | $7.6392 \times 10^{13}$ | $3.9626 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.20 \times 10^{-2}$ |
| $\mathrm{R}(11)$ | 17464.591 | $8.2952 \times 10^{13}$ | $3.7230 \times 10^{-4}$ | $2.46 \times 10^{-37}$ | $2.14 \times 10^{-2}$ |

Table D.13: Band $14^{\prime}-1^{\prime \prime}$ bromine $(79,79)$

| $\mathrm{P}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)$ | 17474.510 | $7.3060 \times 10^{12}$ | $2.3747 \times 10^{-4}$ | $2.82 \times 10^{-37}$ | $2.30 \times 10^{-2}$ |
| $\mathrm{P}(4)$ | 17473.655 | $1.3058 \times 10^{13}$ | $3.8263 \times 10^{-4}$ | $2.11 \times 10^{-37}$ | $2.07 \times 10^{-2}$ |
| $\mathrm{P}(6)$ | 17472.770 | $1.8698 \times 10^{13}$ | $0.7201 \times 10^{-4}$ | $2.25 \times 10^{-37}$ | $1.46 \times 10^{-2}$ |
| $\mathrm{P}(7)$ | 17472.237 | $3.5758 \times 10^{13}$ | $1.8167 \times 10^{-4}$ | $2.85 \times 10^{-37}$ | $2.01 \times 10^{-2}$ |
| $\mathrm{P}(8)$ | 17471.645 | $2.4162 \times 10^{13}$ | $1.0942 \times 10^{-4}$ | $2.60 \times 10^{-37}$ | $2.25 \times 10^{-2}$ |
| $\mathrm{P}(9)$ | 17470.987 | $4.4689 \times 10^{13}$ | $1.8561 \times 10^{-4}$ | $2.37 \times 10^{-37}$ | $2.27 \times 10^{-2}$ |
| $\mathrm{P}(11)$ | 17469.499 | $5.3206 \times 10^{13}$ | $2.3694 \times 10^{-4}$ | $2.52 \times 10^{-37}$ | $2.12 \times 10^{-2}$ |
| $\mathrm{P}(12)$ | 17468.656 | $3.4372 \times 10^{13}$ | $1.5725 \times 10^{-4}$ | $2.58 \times 10^{-37}$ | $2.17 \times 10^{-2}$ |
| $\mathrm{P}(13)$ | 17467.756 | $6.1237 \times 10^{13}$ | $1.5741 \times 10^{-4}$ | $2.27 \times 10^{-37}$ | $2.07 \times 10^{-2}$ |
| $\mathrm{P}(14)$ | 17466.796 | $3.9029 \times 10^{13}$ | $3.0943 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.39 \times 10^{-2}$ |
| $\mathrm{P}(15)$ | 17465.771 | $6.8715 \times 10^{13}$ | $4.5367 \times 10^{-4}$ | $2.06 \times 10^{-37}$ | $2.47 \times 10^{-2}$ |
| $\mathrm{P}(16)$ | 17464.684 | $4.3337 \times 10^{13}$ | $1.9524 \times 10^{-4}$ | $2.51 \times 10^{-37}$ | $2.05 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} \mathrm{J}^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(4)$ | 17474.546 | $1.3058 \times 10^{13}$ | $10.465 \times 10^{-4}$ | $2.82 \times 10^{-37}$ | $2.78 \times 10^{-2}$ |
| $\mathrm{R}(5)$ | 17474.359 | $1.3058 \times 10^{13}$ | $1.5958 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.21 \times 10^{-2}$ |
| $\mathrm{R}(7)$ | 17473.761 | $2.5813 \times 10^{13}$ | $2.5813 \times 10^{-4}$ | $2.12 \times 10^{-37}$ | $1.94 \times 10^{-2}$ |
| $\mathrm{R}(8)$ | 17473.368 | $1.5832 \times 10^{13}$ | $1.5832 \times 10^{-4}$ | $3.00 \times 10^{-37}$ | $2.18 \times 10^{-2}$ |
| $\mathrm{R}(9)$ | 17472.926 | $3.8333 \times 10^{13}$ | $3.8333 \times 10^{-4}$ | $2.38 \times 10^{-37}$ | $2.17 \times 10^{-2}$ |
| $\mathrm{R}(11)$ | 17471.841 | $2.3285 \times 10^{13}$ | $2.3285 \times 10^{-4}$ | $2.23 \times 10^{-37}$ | $1.94 \times 10^{-2}$ |
| $\mathrm{R}(12)$ | 17471.199 | $1.6754 \times 10^{13}$ | $1.6754 \times 10^{-4}$ | $2.53 \times 10^{-37}$ | $2.42 \times 10^{-2}$ |
| $\mathrm{R}(13)$ | 17470.502 | $2.6743 \times 10^{13}$ | $2.6743 \times 10^{-4}$ | $2.28 \times 10^{-37}$ | $1.96 \times 10^{-2}$ |
| $\mathrm{R}(14)$ | 17469.749 | $1.4127 \times 10^{13}$ | $1.4127 \times 10^{-4}$ | $2.22 \times 10^{-37}$ | $1.88 \times 10^{-2}$ |
| $\mathrm{R}(15)$ | 17468.925 | $3.0055 \times 10^{13}$ | $3.0055 \times 10^{-4}$ | $2.78 \times 10^{-37}$ | $2.03 \times 10^{-2}$ |
| $\mathrm{R}(16)$ | 17468.042 | $2.7618 \times 10^{13}$ | $2.7618 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.53 \times 10^{-2}$ |
| $\mathrm{R}(17)$ | 17467.095 | $3.6602 \times 10^{13}$ | $3.6602 \times 10^{-4}$ | $2.54 \times 10^{-37}$ | $2.09 \times 10^{-2}$ |
| $\mathrm{R}(18)$ | 17466.096 | $7.0570 \times 10^{13}$ | $7.0570 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.25 \times 10^{-2}$ |
| $\mathrm{R}(19)$ | 17465.032 | $4.6456 \times 10^{13}$ | $4.6454 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.46 \times 10^{-2}$ |

Table D.14: The unused lines from band $14^{\prime}-1^{\prime \prime}$ bromine $(79,79)$

| $\mathrm{P}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m \nu^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(2)$ | 17474.273 | $7.4295 \times 10^{12}$ | $1.0087 \times 10^{-4}$ | $9.34 \times 10^{-37}$ | $2.36 \times 10^{-2}$ |
| $\mathrm{P}(3)$ | 17473.990 | $1.6980 \times 10^{13}$ | $1.0253 \times 10^{-4}$ | $3.81 \times 10^{-37}$ | $2.58 \times 10^{-2}$ |
| $\mathrm{P}(5)$ | 17473.234 | $2.6494 \times 10^{13}$ | $1.7751 \times 10^{-4}$ | $3.98 \times 10^{-37}$ | $2.80 \times 10^{-2}$ |
| $\mathrm{P}(10)$ | 17470.271 | $2.9402 \times 10^{13}$ | $2.9105 \times 10^{-4}$ | $5.62 \times 10^{-37}$ | $0.83 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m \nu^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(6)$ | 17474.090 | $1.2210 \times 10^{13}$ | $1.2210 \times 10^{-4}$ | $3.28 \times 10^{-37}$ | $1.94 \times 10^{-2}$ |
| $\mathrm{R}(10)$ | 17472.412 | $2.4368 \times 10^{13}$ | $2.4368 \times 10^{-4}$ | $4.27 \times 10^{-37}$ | $2.09 \times 10^{-2}$ |

Table D.15: The unused lines from band $14^{\prime}-1^{\prime \prime}$ bromine $(79,81)$

| $\mathrm{P}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu c m^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(2)$ | 17466.989 | $1.8943 \times 10^{13}$ | $0.9814 \times 10^{-4}$ | $3.70 \times 10^{-37}$ | $2.86 \times 10^{-2}$ |
| $\mathrm{R}(J)$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu c m^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(1)$ | 17467.493 | $1.1383 \times 10^{13}$ | $2.7633 \times 10^{-4}$ | $0.65 \times 10^{-37}$ | $2.94 \times 10^{-2}$ |
| $\mathrm{R}(2)$ | 17467.493 | $1.8943 \times 10^{13}$ | $2.7633 \times 10^{-4}$ | $0.65 \times 10^{-37}$ | $2.94 \times 10^{-2}$ |

## Appendix E

Identified and unused lines of Band $17^{\prime}-2^{\prime \prime}$

Table E.16: Band $17^{\prime}-2^{\prime \prime}$ bromine $(81,81)$

| $\mathrm{P}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)$ | 17465.821 | $1.5504 \times 10^{12}$ | $1.3772 \times 10^{-4}$ | $2.06 \times 10^{-37}$ | $2.27 \times 10^{-2}$ |
| $\mathrm{P}(3)$ | 17465.312 | $3.6068 \times 10^{12}$ | $1.5765 \times 10^{-4}$ | $2.54 \times 10^{-37}$ | $1.92 \times 10^{-2}$ |
| $\mathrm{P}(4)$ | 17464.969 | $2.7715 \times 10^{12}$ | $4.5523 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.59 \times 10^{-2}$ |
| $\mathrm{P}(5)$ | 17464.554 | $5.6241 \times 10^{12}$ | $2.6528 \times 10^{-4}$ | $2.01 \times 10^{-37}$ | $2.19 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(1)$ | 17466.096 | $1.5504 \times 10^{12}$ | $7.0570 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.25 \times 10^{-2}$ |
| $\mathrm{R}(3)$ | 17465.965 | $3.6038 \times 10^{12}$ | $2.2497 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.19 \times 10^{-2}$ |
| $\mathrm{R}(4)$ | 17465.821 | $2.7715 \times 10^{12}$ | $1.3772 \times 10^{-4}$ | $2.06 \times 10^{-37}$ | $2.27 \times 10^{-2}$ |
| $\mathrm{R}(6)$ | 17465.312 | $3.9696 \times 10^{12}$ | $1.5765 \times 10^{-4}$ | $2.54 \times 10^{-37}$ | $1.92 \times 10^{-2}$ |
| $\mathrm{R}(7)$ | 17464.969 | $7.5930 \times 10^{12}$ | $4.5523 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.59 \times 10^{-2}$ |
| $\mathrm{R}(8)$ | 17464.554 | $5.1316 \times 10^{12}$ | $2.6528 \times 10^{-4}$ | $2.01 \times 10^{-37}$ | $2.19 \times 10^{-2}$ |

Table E.17: Band $17^{\prime}-2^{\prime \prime}$ bromine $(79,79)$

| $\mathrm{P}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{\text {mv }{ }^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu c m^{-2}$ | $R_{e}$ | $\Delta \nu \mathrm{cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)$ | 17478.173 | $1.5369 \times 10^{12}$ | $0.9337 \times 10^{-4}$ | $2.62 \times 10^{-}$ | $0^{-2}$ |
| $\mathrm{P}(2)$ | 17477.944 | $1.5345 \times 10^{12}$ | $1.6993 \times 10^{-4}$ | $2.66 \times 10^{-}$ | $2.25 \times 10^{-2}$ |
| $\mathrm{P}(4)$ | 17477.285 | $2.7469 \times 10^{12}$ | $2.0088 \times 10^{-4}$ | $2.19 \times 10^{-}$ | $2.89 \times 10^{-2}$ |
| $P(5)$ | 17476.860 | $5.5735 \times 10^{12}$ | $2.4222 \times 10^{-4}$ | $2.65 \times 10^{-}$ | $2.31 \times 10^{-2}$ |
| $\mathrm{P}(6)$ | 17476.377 | $3.9335 \times 10^{12}$ | $2.9861 \times 10^{-4}$ | $2.52 \times 10$ | $2.72 \times 10^{-2}$ |
| $P(7)$ | 17475.815 | $7.5228 \times 10^{12}$ | $1.5628 \times 10^{-4}$ | $2.06 \times 10$ | $1.79 \times 10^{-2}$ |
| $\mathrm{P}(8)$ | 17475.190 | $5.0834 \times 10^{12}$ | $4.0474 \times 10^{-4}$ | $2.74 \times 10$ | $3.03 \times 10^{-2}$ |
| $\mathrm{P}(9)$ | 17474.510 | $9.4022 \times 10^{12}$ | $2.3747 \times 10^{-4}$ | $2.82 \times 10$ | $2.30 \times 10^{-2}$ |
| $\mathrm{P}(10)$ | 17473.761 | $6.1862 \times 10^{12}$ | $2.5813 \times 10^{-4}$ | $2.11 \times 10$ | $1.94 \times 10^{-2}$ |
| $\mathrm{P}(11)$ | 17472.956 | $1.1195 \times 10^{13}$ | $2.5975 \times 10^{-4}$ | $2.77 \times 10$ | $2.03 \times 10^{-2}$ |
| $\mathrm{P}(14)$ | 17470.118 | $8.2130 \times 10^{12}$ | $1.3608 \times 10$ | $2.34 \times 10$ | $1.62 \times 10$ |
| $\mathrm{P}(15)$ | 17469.035 | $1.4460 \times 10^{13}$ | $3.0989 \times 10$ | $2.78 \times 10$ | $2.06 \times 10^{-2}$ |
| $\mathrm{P}(17)$ | 17466.680 | $1.5907 \times 10^{13}$ | $3.5484 \times 10$ | $2.89 \times 10$ | $2.18 \times 10^{-2}$ |
| $\mathrm{P}(18)$ | 17465.402 | $9.9478 \times 10^{12}$ | $4.2071 \times 10^{-4}$ | 2.42 | 2.09 |
| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ |  | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $R_{e}$ | $\Delta \nu \mathrm{cm}$ |
| $\mathrm{R}(0)$ | 17478.438 | $3.0762 \times 10$ | $0.5719 \times 10$ | $2.66 \times 10$ | $2.12 \times 10^{-2}$ |
| $\mathrm{R}(2)$ | 17478.438 | $1.5345 \times 10^{12}$ | $0.5719 \times 10$ | $2.66 \times 10$ | $2.12 \times 10^{-2}$ |
| $\mathrm{R}(4)$ | 17478.173 | $2.7469 \times 10^{12}$ | $0.9337 \times 10$ | $2.62 \times 10$ | $2.23 \times 10^{-2}$ |
| R(5) | 17477.944 | $5.5735 \times 10^{12}$ | $1.6993 \times 10$ | $2.66 \times 10^{-3}$ | $2.25 \times 10^{-2}$ |
| $\mathrm{R}(7)$ | 17477.285 | $7.5228 \times 10^{12}$ | $2.0088 \times 10^{-4}$ | $2.19 \times 10^{-37}$ | $2.81 \times 10^{-2}$ |
| R(8) | 17476.860 | $5.0843 \times 10^{12}$ | $2.4222 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.12 \times 10^{-2}$ |
| R(9) | 17476.377 | $9.4022 \times 10^{12}$ | $2.9861 \times 10^{-4}$ | $2.52 \times 10^{-3}$ | $2.68 \times 10^{-2}$ |
| $\mathrm{R}(10)$ | 17475.815 | $6.1862 \times 10^{12}$ | $1.5628 \times 10^{-4}$ | $2.06 \times 10^{-}$ | $1.79 \times 10^{-2}$ |
| R(11) | 17475.190 | $1.1195 \times 10^{13}$ | $4.0474 \times 10^{-4}$ | $2.74 \times 10^{-}$ | $3.03 \times 10^{-2}$ |
| $\mathrm{R}(12)$ | 17474.510 | $7.2323 \times 10^{12}$ | $2.3747 \times 10^{-4}$ | $2.82 \times 10^{-}$ | $2.30 \times 10^{-2}$ |
| R(14) | 17472.926 | $8.2130 \times 10^{12}$ | $3.8333 \times 10$ | $2.38 \times 10^{-}$ | $2.17 \times 10^{-2}$ |
| $\mathrm{R}(15)$ | 17472.050 | $1.4460 \times 10^{13}$ | $5.6018 \times 10$ | $2.62 \times 10$ | $2.30 \times 10^{-2}$ |
| $\mathrm{R}(16)$ | 17471.094 | $9.1203 \times 10$ | 2.4579 | 2.99 | $2.06 \times 10^{-2}$ |
| R(17) | 17470.089 | $1.5907 \times 10^{13}$ | $3.3296 \times 10^{-4}$ | $2.34 \times 10^{-}$ | $2.13 \times 10^{-2}$ |
| $\mathrm{R}(18)$ | 17469.002 | $9.9478 \times 10^{12}$ | $3.1130 \times 10^{-4}$ | $2.78 \times 10^{-37}$ | $2.32 \times 10^{-2}$ |
| R(19) | 17467.860 | $1.7216 \times 10^{13}$ | $3.7253 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.03 \times 10^{-2}$ |
| $\mathrm{R}(20)$ | 17466.645 | $1.0690 \times 10^{13}$ | $4.9965 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.02 \times 10^{-2}$ |
| $\mathrm{R}(21)$ | 17465.361 | $1.8379 \times 10^{13}$ | $2.4221 \times 10^{-4}$ | $2.47 \times 10^{-37}$ | $2.11 \times 10^{-2}$ |

Table E.18: Band $17^{\prime}-2^{\prime \prime}$ bromine $(79,81)$

|  |  |  | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left.R_{e}\right\|^{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(1)$ | 1747 |  | 6018×10 | $\times 10$ | $2.30 \times 10^{-2}$ |
| P (2) | 17471.819 | 4.0235 | 2.766 | 2.5 |  |
| $\mathrm{P}(3)$ | 222 | $5.6197 \times 10^{12}$ | 3.504 | 2.54 |  |
| 4) | 17471.166 | $7.2029 \times 10^{12}$ | $4.0899 \times 10^{-1}$ | 2.49 | 2.1 |
|  | 17470.745 | $8.7694 \times 10^{12}$ | $5.2775 \times 10^{-1}$ | 2.76 | 2.14 |
|  | 17469.724 | 1.1838 | $378 \times 10$ | 2.22 | 2.02 |
|  | 106 | 1.3333 | 8.4040 | . 78 | $2.61 \times 10^{-2}$ |
|  | 174 | $1.4798 \times 10^{13}$ | $7.3152 \times 10$ | $2.51 \times 10$ | 2.2 |
|  | 17467.692 | $1.6229 \times 10^{12}$ | $8.3822 \times 10^{-4}$ | $2.27 \times 10$ | $2.49 \times 10^{-2}$ |
|  | 17466 | $1.7623 \times 10^{13}$ | $8.2927 \times 10^{-}$ | $2.45 \times 10$ | 2.51 |
| $\mathrm{P}(12)$ | 17466.015 | 7 | 9.809 | 2.6 | $2.74 \times 10^{-2}$ |
| P (13) | 17465.080 | 289 | $11.5934 \times 10^{-4}$ | $2.89 \times 1$ | 2.90 |
| R(J) | $\nu \mathrm{cm}^{-1}$ |  | $\int k{ }^{\text {d }} \mathrm{cm}^{-2}$ | $R_{e}$ | $\Delta \nu \mathrm{cm}^{-1}$ |
|  | 17472.201 | $6197 \times 10^{12}$ | $1.4712 \times 10^{-4}$ | $\times 10^{-}$ | $1.83 \times 10^{-2}$ |
|  | 17472.050 | 7.2029 | $5.6018 \times 10^{-4}$ | $2.62 \times 10^{-}$ | $2.30 \times 10^{-2}$ |
|  | 17471.819 | 8.769 | 2.7 | 2.5 | 1.9 |
|  | 17471.522 | 1.0316 | $3.5042 \times 10^{-1}$ | 2.54 | 2.04 |
|  | 17471.166 | 1.1838 | $4.0899 \times 10^{-4}$ | 2.49 | 2.12 |
|  | 17470.745 | $1.3333 \times 10^{13}$ | $5.2775 \times 10^{-4}$ | 2.76 | $2.14 \times 10^{-}$ |
|  | 17 | $1.6229 \times 10^{13}$ | $5.6378 \times 10^{-4}$ | 2.22 | 2.0 |
|  | 17469 | $1.7623 \times 10^{13}$ | $8.4040 \times 10^{-1}$ | $2.78 \times 10$ | $2.61 \times 10^{-2}$ |
|  | 17 | 1.8 | 7.3152 | 2.51 | 2.27 |
| R(13) | 17467.692 | 2.0289 | $8.3822 \times 10^{-}$ | 2.2 | 2.4 |
| R(15) | 17466.880 | $2.1556 \times 10^{13}$ | $8.2927 \times 10^{-4}$ | $2.45 \times 10$ | $2.51 \times 10^{-2}$ |
|  | 17466.015 | $2.2775 \times 10^{13}$ | $9.8095 \times 10^{-4}$ | $2.65 \times 10^{-3}$ | $2.74 \times 10^{-2}$ |
| $\mathrm{R}(16)$ | 17 | $2.3945 \times 10^{13}$ | $11.593 \times 10^{-4}$ | $2.89 \times 10^{-}$ | $2.90 \times$ |

Table E.19: The unused lines from band $17^{\prime}-2^{\prime \prime}$ bromine ( 79,79 )

| $\mathrm{P}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(3)$ | 17477.652 | $3.5720 \times 10^{13}$ | $1.5972 \times 10^{-4}$ | $5.24 \times 10^{-37}$ | $2.89 \times 10^{-2}$ |
| $\mathrm{P}(13)$ | 17471.120 | $1.2886 \times 10^{13}$ | $3.5037 \times 10^{-4}$ | $3.23 \times 10^{-37}$ | $2.57 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(1)$ | 17478.461 | $1.5369 \times 10^{12}$ | $1.5994 \times 10^{-4}$ | $8.92 \times 10^{-37}$ | $2.61 \times 10^{-2}$ |
| $\mathrm{R}(3)$ | 17478.337 | $3.5720 \times 10^{12}$ | $1.1779 \times 10^{-4}$ | $3.30 \times 10^{-37}$ | $2.39 \times 10^{-2}$ |
| $\mathrm{R}(6)$ | 17477.652 | $3.9335 \times 10^{12}$ | $1.5628 \times 10^{-4}$ | $5.24 \times 10^{-37}$ | $2.89 \times 10^{-2}$ |

Table E.20: The unused lines from band $17^{\prime}-2^{\prime \prime}$ bromine $(79,81)$

| $\mathrm{P}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m \nu^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(6)$ | 1747.271 | $1.0316 \times 10^{13}$ | $2.9105 \times 10^{-4}$ | $1.34 \times 10^{-37}$ | $2.11 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(0)$ | 17472.276 | $8.0657 \times 10^{12}$ | $11.584 \times 10^{-4}$ | $20.8 \times 10^{-37}$ | $2.07 \times 10^{-2}$ |
| $\mathrm{R}(1)$ | 17472.330 | $2.4178 \times 10^{12}$ | $1.3005 \times 10^{-4}$ | $4.51 \times 10^{-37}$ | $2.16 \times 10^{-2}$ |
| $\mathrm{R}(2)$ | 17472.276 | $4.0235 \times 10^{12}$ | $11.584 \times 10^{-4}$ | $20.8 \times 10^{-37}$ | $2.07 \times 10^{-2}$ |
| $\mathrm{R}(9)$ | 17470.271 | $1.4798 \times 10^{13}$ | $2.9105 \times 10^{-4}$ | $1.34 \times 10^{-37}$ | $2.11 \times 10^{-2}$ |

Table E.21: The unused lines from band $17^{\prime}-2^{\prime \prime}$ bromine $(81,81)$

| $\mathrm{P}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu c m^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(2)$ | 17465.597 | $1.5480 \times 10^{12}$ | $2.0183 \times 10^{-4}$ | $3.09 \times 10^{-37}$ | $2.11 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu c m^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(5)$ | 17465.597 | $5.9624 \times 10^{12}$ | $2.0183 \times 10^{-4}$ | $3.09 \times 10^{-37}$ | $2.11 \times 10^{-2}$ |

## Appendix $\mathbf{F}$

Identified and unused lines of Band $18^{\prime}-2^{\prime \prime}$

Table F.22: Band $18^{\prime}-2^{\prime \prime}$ bromine (79,79)

| $\mathrm{P}(\mathrm{J})$ | $\nu c \mathrm{~cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(53)$ | 17477.072 | $1.7786 \times 10^{13}$ | $4.7254 \times 10^{-4}$ | $2.96 \times 10^{-37}$ | $2.45 \times 10^{-2}$ |
| $\mathrm{P}(54)$ | 17473.334 | $1.0419 \times 10^{13}$ | $4.7261 \times 10^{-4}$ | $3.00 \times 10^{-37}$ | $2.41 \times 10^{-2}$ |
| $\mathrm{P}(55)$ | 17469.532 | $1.6935 \times 10^{13}$ | $3.6368 \times 10^{-4}$ | $2.40 \times 10^{-37}$ | $1.99 \times 10^{-2}$ |
| $\mathrm{P}(56)$ | 17465.655 | $9.8985 \times 10^{12}$ | $5.8730 \times 10^{-4}$ | $2.70 \times 10^{-37}$ | $2.25 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu c \mathrm{~cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(56)$ | 17476.356 | $9.8985 \times 10^{12}$ | $2.4532 \times 10^{-4}$ | $2.72 \times 10^{-37}$ | $2.09 \times 10^{-2}$ |
| $\mathrm{R}(57)$ | 17472.602 | $1.6054 \times 10^{13}$ | $3.4534 \times 10^{-4}$ | $2.36 \times 10^{-37}$ | $2.09 \times 10^{-2}$ |
| $\mathrm{R}(59)$ | 17464.869 | $1.5152 \times 10^{13}$ | $3.2013 \times 10^{-4}$ | $2.32 \times 10^{-37}$ | $1.88 \times 10^{-2}$ |

Table F.23: Band $18^{\prime}-2^{\prime \prime}$ bromine $(79,81)$

| $\mathrm{P}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu c m^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(51)$ | 17479.440 | $2.9630 \times 10^{13}$ | $7.1115 \times 10^{-4}$ | $2.62 \times 10^{-37}$ | $2.17 \times 10^{-2}$ |
| $\mathrm{P}(52)$ | 17475.897 | $2.9010 \times 10^{13}$ | $6.2008 \times 10^{-4}$ | $2.06 \times 10^{-37}$ | $2.02 \times 10^{-2}$ |
| $\mathrm{P}(54)$ | 17468.593 | $2.7713 \times 10^{13}$ | $5.7247 \times 10^{-4}$ | $2.31 \times 10^{-37}$ | $1.88 \times 10^{-2}$ |
| $\mathrm{P}(55)$ | 17464.843 | $2.7041 \times 10^{13}$ | $5.7254 \times 10^{-4}$ | $2.37 \times 10^{-37}$ | $1.88 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m \nu}{ }^{\prime \prime} J^{\prime \prime}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(54)$ | 17478.826 | $2.7713 \times 10^{13}$ | $5.5294 \times 10^{-4}$ | $2.19 \times 10^{-37}$ | $2.06 \times 10^{-2}$ |
| $\mathrm{R}(55)$ | 17475.257 | $2.7041 \times 10^{13}$ | $10.7176 \times 10^{-4}$ | $2.74 \times 10^{-37}$ | $2.51 \times 10^{-2}$ |
| $\mathrm{R}(56)$ | 17471.616 | $2.6356 \times 10^{13}$ | $6.9485 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.37 \times 10^{-2}$ |
| $\mathrm{R}(57)$ | 17467.919 | $2.5661 \times 10^{13}$ | $6.5901 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.21 \times 10^{-2}$ |

Table F.24: Band $18^{\prime}-2^{\prime \prime}$ bromine $(81,81)$

| $\mathrm{P}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(50)$ | 17477.867 | $1.1775 \times 10^{13}$ | $2.2091 \times 10^{-4}$ | $2.14 \times 10^{-37}$ | $1.81 \times 10^{-2}$ |
| $\mathrm{P}(52)$ | 17470.934 | $1.1311 \times 10^{13}$ | $2.2259 \times 10^{-4}$ | $2.25 \times 10^{-37}$ | $2.22 \times 10^{-2}$ |
| $\mathrm{P}(53)$ | 17467.375 | $1.8845 \times 10^{13}$ | $3.6337 \times 10^{-4}$ | $2.25 \times 10^{-37}$ | $1.98 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(53)$ | 17477.315 | $1.8445 \times 10^{13}$ | $4.7498 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $1.79 \times 10^{-2}$ |
| $\mathrm{R}(54)$ | 17473.862 | $1.0816 \times 10^{13}$ | $2.6044 \times 10^{-4}$ | $2.70 \times 10^{-37}$ | $1.88 \times 10^{-2}$ |
| $\mathrm{R}(55)$ | 17470.360 | $1.7599 \times 10^{13}$ | $3.4489 \times 10^{-4}$ | $2.20 \times 10^{-37}$ | $1.94 \times 10^{-2}$ |
| $\mathrm{R}(56)$ | 17466.783 | $1.0298 \times 10^{13}$ | $3.1334 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.45 \times 10^{-2}$ |

Table F.25: The unused lines from band $18^{\prime}-2^{\prime \prime}$ bromine $(79,7.9)$

| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{R}(58)$ | 17468.766 | $9.3629 \times 10^{12}$ | $3.0098 \times 10^{-4}$ | $3.53 \times 10^{-37}$ | $2.35 \times 10^{-2}$ |

Table F.26: The unused lines from band $18^{\prime}-2^{\prime \prime}$ bromine $(79,81)$

| $\mathrm{P}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(53)$ | 17472.276 | $2.8370 \times 10^{13}$ | $11.5838 \times 10^{-4}$ | $20.8 \times 10^{-37}$ | $2.07 \times 10^{-2}$ |

Table F.27: The unused lines from band $18^{\prime}-2^{\prime \prime}$ bromine $(81,81)$

| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m \nu^{\prime \prime} \mathrm{J}^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{R}(51)$ | 17474.434 | $1.9245 \times 10^{13}$ | $5.2880 \times 10^{-4}$ | $3.14 \times 10^{-37}$ | $2.22 \times 10^{-2}$ |

## Appendix G

Identified and unused lines of Band $19^{\prime}-2^{\prime \prime}$

Table G.28: Band $19^{\prime}-2^{\prime \prime}$ bromine ( 79,79 )

| $\mathrm{P}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(74)$ | 17475.310 | $5.1682 \times 10^{12}$ | $0.3988 \times 10^{-4}$ | $2.74 \times 10^{-37}$ | $2.27 \times 10^{-2}$ |
| $\mathrm{P}(75)$ | 17469.938 | $8.2301 \times 10^{12}$ | $2.0805 \times 10^{-4}$ | $2.80 \times 10^{-37}$ | $2.31 \times 10^{-2}$ |
| $\mathrm{P}(76)$ | 17464.554 | $4.7136 \times 10^{12}$ | $2.6528 \times 10^{-4}$ | $2.01 \times 10^{-37}$ | $2.19 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(76)$ | 17488.640 | $4.7136 \times 10^{12}$ | $1.8104 \times 10^{-4}$ | $2.67 \times 10^{-37}$ | $2.32 \times 10^{-2}$ |
| $\mathrm{R}(77)$ | 17473.368 | $7.4919 \times 10^{12}$ | $1.5832 \times 10^{-4}$ | $3.00 \times 10^{-37}$ | $2.18 \times 10^{-2}$ |
| $\mathrm{R}(78)$ | 17467.982 | $4.2828 \times 10^{12}$ | $0.9802 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.34 \times 10^{-2}$ |

Table G.29: Band $19^{\prime}-2^{\prime \prime}$ bromine $(79,81)$

| $\mathrm{P}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(73)$ | 17477.024 | $1.4541 \times 10^{13}$ | $2.8446 \times 10^{-4}$ | $2.16 \times 10^{-37}$ | $2.03 \times 10^{-2}$ |
| $\mathrm{P}(74)$ | 17471.862 | $1.3917 \times 10^{13}$ | $3.1012 \times 10^{-4}$ | $2.46 \times 10^{-37}$ | $1.94 \times 10^{-2}$ |
| $\mathrm{P}(75)$ | 17466.607 | $1.3307 \times 10^{13}$ | $3.0955 \times 10^{-4}$ | $2.89 \times 10^{-37}$ | $2.00 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(76)$ | 17475.257 | $1.2711 \times 10^{13}$ | $10.7176 \times 10^{-4}$ | $2.74 \times 10^{-37}$ | $2.51 \times 10^{-2}$ |
| $\mathrm{R}(77)$ | 17470.058 | $1.2131 \times 10^{13}$ | $2.4787 \times 10^{-4}$ | $2.34 \times 10^{-37}$ | $1.91 \times 10^{-2}$ |
| $\mathrm{R}(78)$ | 17464.769 | $1.1566 \times 10^{13}$ | $6.0178 \times 10^{-4}$ | $2.21 \times 10^{-37}$ | $1.91 \times 10^{-2}$ |

## Appendix H

Identified and unused lines of Band $15^{\prime}-1^{\prime \prime}$

Table H.30: Band $15^{\prime}-1^{\prime \prime}$ bromine (79,79)

| $\mathrm{P}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(57)$ | 17476.913 | $7.5921 \times 10^{13}$ | $4.6382 \times 10^{-4}$ | $2.61 \times 10^{-37}$ | $2.34 \times 10^{-2}$ |
| $\mathrm{P}(58)$ | 17473.141 | $4.4271 \times 10^{13}$ | $2.5729 \times 10^{-4}$ | $2.48 \times 10^{-37}$ | $1.94 \times 10^{-2}$ |
| $\mathrm{P}(59)$ | 17469.309 | $3.9268 \times 10^{13}$ | $2.3394 \times 10^{-4}$ | $2.34 \times 10^{-37}$ | $2.31 \times 10^{-2}$ |
| $\mathrm{P}(60)$ | 17465.411 | $4.1680 \times 10^{13}$ | $2.4221 \times 10^{-4}$ | $2.42 \times 10^{-37}$ | $2.09 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(61)$ | 17473.645 | $6.7295 \times 10^{13}$ | $3.8263 \times 10^{-4}$ | $2.10 \times 10^{-37}$ | $2.07 \times 10^{-2}$ |
| $\mathrm{R}(63)$ | 17465.929 | $6.2957 \times 10^{13}$ | $3.0085 \times 10^{-4}$ | $2.65 \times 10^{-37}$ | $2.23 \times 10^{-2}$ |

Table H.31: Band 15' $-1^{\prime \prime}$ bromine $(79,81)$

| $\mathrm{P}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(55)$ | 17478.132 | $1.2671 \times 10^{14}$ | $6.4400 \times 10^{-4}$ | $2.27 \times 10^{-37}$ | $1.97 \times 10^{-2}$ |
| $\mathrm{P}(56)$ | 17474.530 | $1.2348 \times 10^{14}$ | $10.465 \times 10^{-4}$ | $2.82 \times 10^{-37}$ | $2.78 \times 10^{-2}$ |
| $\mathrm{P}(57)$ | 17470.882 | $1.2020 \times 10^{14}$ | $6.3559 \times 10^{-4}$ | $2.36 \times 10^{-37}$ | $2.19 \times 10^{-2}$ |
| $\mathrm{P}(58)$ | 17467.161 | $1.1689 \times 10^{14}$ | $6.8468 \times 10^{-4}$ | $2.62 \times 10^{-37}$ | $2.20 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(58)$ | 17478.691 | $1.1689 \times 10^{14}$ | $6.4681 \times 10^{-4}$ | $2.67 \times 10^{-37}$ | $2.19 \times 10^{-2}$ |
| $\mathrm{R}(59)$ | 17475.099 | $1.1354 \times 10^{14}$ | $6.0241 \times 10^{-4}$ | $2.33 \times 10^{-37}$ | $1.97 \times 10^{-2}$ |
| $\mathrm{R}(60)$ | 17471.445 | $1.1017 \times 10^{14}$ | $5.5828 \times 10^{-4}$ | $2.23 \times 10^{-37}$ | $2.04 \times 10^{-2}$ |
| $\mathrm{R}(61)$ | 17467.732 | $1.0679 \times 10^{14}$ | $5.9345 \times 10^{-4}$ | $2.27 \times 10^{-37}$ | $2.28 \times 10^{-2}$ |

Table H.32: Band $15^{\prime}-1^{\prime \prime}$ bromine $(81,81)$

| $\mathrm{P}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu c m^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu c m^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(53)$ | 17478.874 | $8.5633 \times 10^{13}$ | $5.1914 \times 10^{-4}$ | $2.71 \times 10^{-37}$ | $2.36 \times 10^{-2}$ |
| $\mathrm{P}(54)$ | 17475.459 | $5.0208 \times 10^{13}$ | $2.7060 \times 10^{-4}$ | $2.41 \times 10^{-37}$ | $2.22 \times 10^{-2}$ |
| $\mathrm{P}(55)$ | 17471.981 | $8.1681 \times 10^{13}$ | $4.0085 \times 10^{-4}$ | $2.19 \times 10^{-37}$ | $2.08 \times 10^{-2}$ |
| $\mathrm{P}(56)$ | 17468.441 | $4.7785 \times 10^{13}$ | $2.4417 \times 10^{-4}$ | $2.28 \times 10^{-37}$ | $2.17 \times 10^{-2}$ |
| $\mathrm{P}(57)$ | 17464.839 | $7.7571 \times 10^{13}$ | $6.0178 \times 10^{-4}$ | $2.21 \times 10^{-37}$ | $1.91 \times 10^{-2}$ |
| $\mathrm{R}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} \mathrm{J}^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| $\mathrm{R}(56)$ | 17479.455 | $4.7785 \times 10^{13}$ | $2.1641 \times 10^{-4}$ | $2.62 \times 10^{-37}$ | $1.90 \times 10^{-2}$ |
| $\mathrm{R}(58)$ | 17472.572 | $4.5283 \times 10^{13}$ | $2.0538 \times 10^{-4}$ | $2.00 \times 10^{-37}$ | $2.07 \times 10^{-2}$ |
| $\mathrm{R}(59)$ | 17469.037 | $7.3353 \times 10^{13}$ | $3.7690 \times 10^{-4}$ | $2.78 \times 10^{-37}$ | $2.26 \times 10^{-2}$ |
| $\mathrm{R}(60)$ | 17465.438 | $4.2731 \times 10^{13}$ | $5.8411 \times 10^{-4}$ | $2.42 \times 10^{-37}$ | $2.11 \times 10^{-2}$ |

Table H.33: The unused lines from band $15^{\prime}-1^{\prime \prime}$ bromine $(79,79)$

| $\mathrm{R}(\mathrm{J})$ | $\nu c m^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{R}(60)$ | 17477.434 | $4.1680 \times 10^{13}$ | $4.3797 \times 10^{-4}$ | $4.41 \times 10^{-37}$ | $4.41 \times 10^{-2}$ |
| $\mathrm{R}(62)$ | 17469.834 | $3.9074 \times 10^{13}$ | $1.6549 \times 10^{-4}$ | $1.78 \times 10^{-37}$ | $1.78 \times 10^{-2}$ |

Table H.34: The unused lines from band $15^{\prime}-1^{\prime \prime}$ bromine $(81,81)$

| $\mathrm{R}(\mathrm{J})$ | $\nu \mathrm{cm}^{-1}$ | $N_{m v^{\prime \prime} J^{\prime \prime}}$ | $\int k_{\nu} d \nu \mathrm{~cm}^{-2}$ | $\left\|R_{e}\right\|^{2}$ | $\Delta \nu \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{R}(57)$ | 17476.045 | $7.7571 \times 10^{13}$ | $1.5676 \times 10^{-4}$ | $0.89 \times 10^{-37}$ | $1.78 \times 10^{-2}$ |

Table H.35: The F.C.F.used for calculating $\left|R_{e}\right|^{2}$

| State | Isotope | Band | F.C.F. |
| :---: | :---: | :---: | :---: |
| $B^{3} \Pi_{o}+u$ | $(79,79) B r_{2}$ | $14^{\prime}-1^{\prime \prime}$ | 0.00509 |
|  | $(79,81) B r_{2}$ | $14^{\prime}-1^{\prime \prime}$ | 0.00408 |
|  | $(79,79) B r_{2}$ | $15^{\prime}-1^{\prime \prime}$ | 0.00650 |
|  | $(79,81) B r_{2}$ | $15^{\prime}-1^{\prime \prime}$ | 0.00621 |
|  | $(81,81) B r_{2}$ | $15^{\prime}-1^{\prime \prime}$ | 0.00594 |
|  | $(79,79) B r_{2}$ | $17^{\prime}-2^{\prime \prime}$ | 0.02405 |
|  | $(79,81) B r_{2}$ | $17^{\prime}-2^{\prime \prime}$ | 0.02378 |
|  | $(81,81) B r_{2}$ | $17^{\prime}-2^{\prime \prime}$ | 0.02324 |
|  | $(79,79) B r_{2}$ | $18^{\prime}-2^{\prime \prime}$ | 0.02487 |
|  | $(79,81) B r_{2}$ | $18^{\prime}-2^{\prime \prime}$ | 0.02478 |
|  | $(81,81) B r_{2}$ | $18^{\prime}-2^{\prime \prime}$ | 0.02429 |
|  | $(79,79) B r_{2}$ | $19^{\prime}-2^{\prime \prime}$ | 0.02504 |
|  | $(79,81) B r_{2}$ | $19^{\prime}-2^{\prime \prime}$ | 0.02511 |

Table H.36: The F.C.F. $\left({ }^{(79,79)} B r_{2}\right)$ used for calculating $\tau_{\text {rad }}$

| Band | F.C.F. | Band | F.C.F. | Band | F.C.F. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 14'-0' | 0.00060 | 17'-0" | 0.00144 | 15'-0" | 0.00083 |
| 14'-1" | 0.00509 | 17'-1" | 0.00951 | 15'1" | 0.00650 |
| 14'-2" | 0.01775 | 17'-2" | 0.02405 | 15'-2" | 0.02040 |
| 14'3" | 0.03145 | 17'3" | 0.02640 | 15'-3" | 0.03111 |
| 14'-4" | 0.02639 | 17'-4" | 0.00812 | 15'-4" | 0.01995 |
| 14'-5" | 0.00543 | 17'-5" | 0.00107 | 15'-6" | 0.00126 |
| 14'-6" | 0.00264 | 17'-6" | 0.01531 | 15'-7" | 0.00731 |
| 14'-7" | 0.01859 | 17'-7' | 0.01233 | 15'-8" | 0.01958 |
| 14'-8" | 0.01447 | 17'-8" | 0.000016 | 15'-9" | 0.00727 |
| 14'-9" | 0.00018 | 17'-9" | 0.01058 | 15'-10" | 0.00133 |
| 14'-10" | 0.01026 | 17'-10" | 0.01235 | 15'-11" | 0.01537 |

Table H.37: The F.C.F. used for calculating $\tau_{\text {rad }}$

| Isotope | Band | F.C.F. | Band | F.C.F. |
| :---: | :---: | :---: | :---: | :---: |
| ${ }^{(79,79)} \mathrm{Br}_{2}$ | 18'0'0' | 0.00180 | 19'-0" | 0.00220 |
|  | 18'-1" | 0.00.99 | 19'-1" | 0.01238 |
|  | 18'-2" | 0.02487 | 19'-2" | 0.02504 |
|  | 18'-3" | 0.02273 | 19'-3" | 0.01876 |
|  | 18'-4" | 0.00400 | 19'-4" | 0.00137 |
|  | 18'-5" | 0.00358 | 19'-5" | 0.00660 |
|  | 18'-6" | 0.01651 | 19'-6" | 0.01571 |
|  | 18'-7" | 0.00726 | 19'-7" | 0.00316 |
|  | 18'-8" | 0.00106 | 19'-8" | 0.00391 |
|  | 18'-9" | 0.01339 | 19'-9" | 0.01348 |
|  | 18'-10" | 0.00712 | 19'-10" | 0.00263 |

Table H.38: The F.C.F. $\left({ }^{(81,81)} B r_{2}\right)$ used for calculating $\tau_{\text {rad }}$

| Band | F.C.F. | Band | F.C.F. | Band | F.C.F. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 18'-0" | 0.00164 | 17'-0" | 0.00130 | 15'-0" | 0.00074 |
| 18'-1" | 0.01030 | 17'-1" | 0.00884 | 15'-1" | 0.00594 |
| 18'2" | 0.02429 | 17'-2" | 0.02324 | 15'-2" | 0.01931 |
| 18'-3" | 0.02378 | 17'-3" | 0.02712 | 15'-3" | 0.03094 |
| 18'-4" | 0.00525 | 17'-4" | 0.00975 | 15'-4" | 0.02173 |
| 18'-5" | 0.00253 | 17'-5" | 0.00048 | 15'-6" | 0.00223 |
| 18'-6" | 0.01608 | 17'6" | 0.01418 | 15'-7" | 0.00565 |
| 18'-7" | 0.00877 | 17'-7' | 0.01384 | 15'-8" | 0.01940 |
| 18'-8" | 0.00041 | 17'-8" | 0.00030 | 15'-9" | 0.00927 |
| 18'-9" | 0.01250 | 17?-9" | 0.00897 | 15'-10" | 0.00048 |
| 18'-10" | 0.00811 | 17'-10" | 0.01326 | 15'-11" | 0.01402 |

Table H.39: The F.C.F. $\left({ }^{(79,81)} B r_{2}\right)$ used for calculating $\tau_{\text {rad }}$

| Band | F.C.F. | Band | F.C.F. | Band | F.C.F. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 14! - 0" | 0.00056 | 17'0" | 0.00138 | 15'0"' | 0.00079 |
| 14'-1" | 0.00482 | 17'-1" | 0.00924 | 15'-1" | 0.00621 |
| 14'-2" | 0.01714 | 17'-2" | 0.02378 | 15'-2" | 0.01985 |
| 14'-3" | 0.03106 | 17'-3" | 0.02684 | 15'-3" | 0.03102 |
| 14'-4" | 0.02715 | 17'-4" | 0.00899 | 15'-4" | 0.02091 |
| 14'-5" | 0.00640 | 17'-5" | 0.00071 | 15'5" | 0.00178 |
| 14'-6" | 0.00198 | 17'-6" | 0.01446 | 15'-6" | 0.00635 |
| 14'-7" | 0.01790 | 17'-7" | 0.01314 | 15'-7" | 0.01952 |
| 14'-8" | 0.01551 | 17'-8" | 0.00013 | 15'-8" | 0.00835 |
| 14'-9" | 0.00046 | 17'-9" | 0.00976 | 15'-9" | 0.00083 |
| 14'-10" | 0.00914 | 17'-10" | 0.01309 | 15'-10" | 0.01472 |
| 14'-11" | 0.01736 | 17'-11" | 0.00045 | 15'-11" | 0.01145 |
| 14'-12" | 0.00327 | 17?-12" | 0.00817 | 15'-12" | 0.000001 |
| 14'-13" | 0.00415 | 17'-13" | 0.01255 | 15'-13" | 0.01126 |
| 14'-14" | 0.01662 | 17'-14" | 0.00055 | 15'-14' | 0.01296 |
| 14'-15" | 0.00640 | 17'-15" | 0.00766 | 15'-15" | 0.00029 |
| 14'-16" | 0.00155 | 17'-16" | 0.01201 | 15'-16" | 0.00896 |
| 14'-17" | 0.01514 | 17'-17" | 0.00044 | 15'-17" | 0.01385 |
| 14'-18" | 0.00930 | 17'-18" | 0.00787 | 15'-18" | 0.00092 |
| 14'-19" | 0.00028 | 17'-19"' | 0.01164 | 15'-19" | 0.00728 |
| 14'-20" | 0.01324 | 17'-20" | 0.00028 | 15'-20" | 0.01451 |

Table H.40: The F.C.F. used for calculating $\tau_{\text {rad }}$

| Isotope | Band | F.C.F. | Band | F.C.F. |
| :---: | :---: | :---: | :---: | :---: |
| ${ }^{(79,81)} \mathrm{Br}_{2}$ | 18'-0" | 0.00175 | 19'-0". | 0.00215 |
|  | 18'-1" | 0.01076 | 19'-1" | 0.01220 |
|  | 18'-2" | 0.02478 | 19'-2" | 0.02511 |
|  | 18'-3" | 0.02334 | 19'-3" | 0.01942 |
|  | 18'-4" | 0.00463 | 19'-4" | 0.00174 |
|  | 18'-5" | 0.00298 | 19'-5" | 0.00593 |
|  | 18'-6" | 0.01624 | 19'-6" | 0.01578 |
|  | 18'-7" | 0.00809 | 19'-7" | 0.00378 |
|  | 18'-8" | 0.00068 | 19'-8" | 0.00326 |
|  | 18-9" | 0.01297 | 19'-9" | 0.01354 |
|  | 18'-10" | 0.00802 | 19'-10" | 0.00331 |
|  | 18'-11" | 0.00051 | 19'-11" | 0.00348 |
|  | 18'-12" | 0.01207 | 19'-12" | 0.01254 |
|  | 18'-13" | 0.00715 | 19'-13" | 0.00220 |

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