The spectroscopy of clusters containing mercury.

Jeff S. Lee
University of Windsor

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UMI
THE SPECTROSCOPY OF CLUSTERS CONTAINING MERCURY

by

Jeff S. Lee

A Thesis
Submitted to the College of Graduate Studies and Research
through the Department of Physics
in Partial Fulfillment of the Requirements for
the Degree of Master of Science at the
University of Windsor

Windsor, Ontario, Canada

1999

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Abstract

Van der Waals clusters involving mercury have been studied in a supersonic expansion beam crossed with a laser. The expansion beam consisted of Argon gas seeded with Hg vapor from a heated reservoir. \( \text{Hg}_m\text{Ar}_n \) and \( \text{Hg}_m \) \((m, n \geq 1)\) clusters were produced in the beam by collisional mechanisms.

In this thesis, previously unobserved fluorescence spectra were observed for several different laser excitation wavelengths. Five of these wavelengths, 2534.3 Å, 2534.6 Å, 2535.8 Å, 2536.0 Å and 2537.2 Å, corresponded to clearly defined absorption wavelengths in the excitation spectrum. The sixth wavelength at 2533.7 Å corresponded to a plateau in the excitation spectrum.

None of these fluorescence spectra can be assigned to definite transitions at this moment, although three of them are probably due to \( \text{Hg}_2\text{Ar} \) and correspond to transitions from various vibrational states of an excited electronic excited state to various vibrational levels of the ground electronic state. One fluorescence spectrum is probably due to \( \text{Hg}_3 \), but the remaining two fluorescence spectra clearly require further study.
Acknowledgements

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I would further like to express my appreciation to Mr. S. Jezdic for all of his assistance with the computer and electronics assembly required for my experiment.

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A2.1 Supersonic gas expansion. The flow is subsonic in the gas source, and supersonic in the zone of silence.
Chapter 1

Introduction
1 Introduction

Over the last 15 years, diatomic molecules such as Hg₂ and HgRG (RG is one of the rare gases He, Ne, Ar, Kr, and Xe) that were created in supersonic expansion beams have been studied extensively, including low energy electronic states of HgRG [1, 2], HgArₙ (n ≤ 4) [3, 4], and Hg₂ [5 - 10].

Although the spectroscopy of Ag₂RG [11] clusters, and Hgₙ (n > 6) [12, 13] clusters in supersonic expansion beams have been reported in the literature as early as 1991, it wasn’t until 1998 that the spectra of Hg₂RG clusters were observed [14]. Hg₃ spectra have been observed in vapor cells, but this was confined to emission at 4850 Å [15,16], and a fluorescence band at 2170 Å that arises because of a Hg₃ absorption band [17]. Only Crepin and Tramer [18] report a spectrum of Hg₃ resulting from the trimer being trapped in a rare gas matrix.

Koperski et. al. [14] reported the first observed excitation and fluorescence spectra of Hg₂Ar, Hg₂Kr and Hg₃ formed in a supersonic expansion beam. On the short wavelength side of the Hg atomic line, a series of new peaks have been observed and ascribed to Hg₂Ar. A single new peak on the long wavelength side of the atomic line was also observed, and was most likely due to Hg₃.

The most intense Hg₂Ar peak in this spectral region is located at 2535.8 Å, and the new single Hg₃ peak is located at 2537.2 Å. In this research, these peaks were laser excited, and their fluorescence spectra were observed.

The conditions in the supersonic expansion beam are vital to the production of these small poly-atomic clusters. The clustering process and interaction between the
laser and molecules are important considerations in the design of this experiment, and are described in the following sections.

1.1 Supersonic Beams

To create a supersonic beam, gas under high pressure must pass through a nozzle into a region of very low pressure. After passing through the nozzle, the gas cools considerably due to the expansion equalizing the random molecular velocities that existed prior to the expansion. As the nozzle diameter is much greater than the mean free path of the molecules, a great number of collisions occur while the gas expands.

A simple treatment of the expansion requires several assumptions: (i) clustering does not occur in the beam, (ii) heat conduction can be ignored, (iii) beam turbulence can be ignored. Therefore, the total enthalpy of the gas at rest is converted entirely into kinetic energy. Realizing that \( c_p = 5k/2 \) (for atoms), the following results:

\[
T = \frac{T_o}{1 + \frac{1}{2}(\gamma - 1)M^2}
\]  

where \( \gamma = c_p/c_v \), \( M \) is the local Mach number \( (v/\sqrt{\gamma kT/m})^{1/2} \), \( T \) is the local temperature along any streamline of the gas during expansion, and \( T_o \) is the temperature of the gas prior to expansion.

It is important to note that the velocities in a supersonic beam are comparable to the velocities in an effusive source. However, in a supersonic beam, the gas velocities are in excess of the local speed of sound, hence the term supersonic.
For an atomic beam, the maximum possible speed of the gas atoms is \((5kT_0/m)^{1/2}\).

Assuming an isentropic flow (i.e., entropy is conserved along all streamlines), adiabatic expansion occurs, and therefore:

\[
\frac{P}{P_0} = \frac{\rho}{\rho_0} = \frac{T}{T_0}
\]  

(1.2)

and subsequently:

\[
\frac{T}{T_0} = \left(1 + \frac{1}{2} (\gamma - 1)M^2 \right)^{-1}
\]

\[
\frac{\rho}{\rho_0} = \left(1 + \frac{1}{2} (\gamma - 1)M^2 \right)^{\frac{1}{\gamma - 1}}
\]  

(1.3a,b,c)

\[
\frac{P}{P_0} = \left(1 + \frac{1}{2} (\gamma - 1)M^2 \right)^{\frac{1}{\gamma - 1}}
\]

where \(T, \rho, P\) are the local temperature, density, and pressure respectively, and \(T_0, \rho_0, P_0\) are the stagnation temperature, density, and pressure respectively.

The temperature, density, and pressure anywhere in the supersonic beam can be calculated, only if the local Mach number is known. The local Mach number is dependent on the reduced distance \(x/D\) (\(x\) is the distance from the nozzle aperture along the beam axis; \(D\) is the aperture diameter), and the specific heat capacity ratio \(\gamma\). The local Mach number increases with increasing \(\gamma\) and increasing \(x/D\). The width of the velocity distribution narrows with an increasing local Mach number, however the mean velocity changes very little. Table 1.1 shows the temperature and pressure within a supersonic beam for several reduced distances [19].

At the point in the beam where collisions cease due to the drop in pressure and density, the expansion can no longer be regarded as continuous. As all the characteristics
of a continuum freeze at this "front", this location in the beam has been termed the

*Freezing Surface.*

The location of the Mach disk is largely independent of $\gamma$ and is given by 1.4 [20]:

\[
\frac{x_M}{D} = 0.67 \left( \frac{P_o}{P} \right)^{\frac{1}{2}}
\]  

(1.4)

where $x_M/D$ is the reduced distance where the Mach disk is located, $P_o$ is the nozzle
(stagnation) pressure, and $P$ is the background pressure in the chamber.

It should be noted that in a pulsed expansion, the mass flow rate $(dm/dt)$ through
the nozzle varies with time, and is a maximum at half the pulse length. As a result, the
distribution of the sizes of any clusters formed is time dependent throughout the pulse.
<table>
<thead>
<tr>
<th>Reduced Distance (x/D)</th>
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<td>10</td>
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<td>1.6</td>
<td>2</td>
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<td>30</td>
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Table 1.1 The axial temperatures and pressures in a supersonic beam of Helium at 300 K expanded under a pressure of 10 atm into a vacuum.
1.2 Clustering

The formation of clusters for this research was accomplished by the method of aerodynamic acceleration by a seeded beam. This technique has the ability to produce beams with energies between 1 eV and 20 eV. In this method, a relatively small number of heavy particles (in this case Mercury) are combined with a large number of lighter particles (in this case Argon).

This beam of Argon and Mercury is passed through a pulsed valve into a vacuum chamber with a background pressure less than 0.01 torr. There are several advantages to using pulsed valves. Pulsed beams use less carrier and seed gases than do continuous beams. Furthermore, a smaller vacuum pump can be used with pulsed valves. As a result, the instantaneous beam intensities are higher, as well as an increased cluster content.

There are however two disadvantages to using pulsed valves over a continuous beam. A pulsed valve has a lower duty cycle, although this is rarely an issue given that current experiments use pulsed lasers and pulsed detection systems with much lower duty cycles. However, the beam from a pulsed valve has much less uniformity in temperature, beam velocity, and in the distribution of clusters.

Times between 50 μs and 1000 μs are typical pulse durations. At an operating frequency of 10 Hz, the time between pulses greatly exceeds this range of pulse durations. A minimum opening time for a pulse valve can be identified as the minimum time required for the terminal temperature to become independent of the pulse length, and is given by:

\[ \tau_{\text{min}} = \tau_a + \tau_{\text{exp}} + \tau_{\text{eq}} \]  

(1.5)
where $\tau_{\text{min}}$ is the minimum opening time, $\tau_a$ is the time required for the gas behind the nozzle to exit the nozzle, $\tau_{\text{exp}}$ is the time required for an expansion buffer to form beyond the nozzle, and $\tau_{\text{eq}}$ is the time required for the expansion buffer to equilibrate.

In the case of 2000 torr of Argon flowing through a cylindrical nozzle with a 0.5 mm aperture, the minimum opening time is 15.1 $\mu$s [21].

If the beam's concentration of heavy species is very low, then the energy of the heavy species is approximately $T_H M_H/M_L$ ($M_H$ is the molecular mass of the heavy molecule, $M_L$ is the molecular mass of the light molecule, and $T_H$ is the kinetic energy of the heavy molecule expanded in the absence of the light molecule). This result assumes that with the exception of kinetic energy, the heavier molecule makes no contribution to the specific heat of the lighter molecule. Also assumed is a totally isentropic expansion of the beam for all Mach numbers.

The high energy that results from the $T_H M_H/M_L$ product carries with it a disadvantage. There is a loss of beam intensity. However, the intensity gains provided by a nozzle are much higher than those provided by an effusive source. This is true even if the number of heavy molecules in the effusive source is 100 times greater than the number of heavy molecules in the beam from a nozzle. In addition, the higher effective Mach number of the heavy molecules results in their concentration along the beam axis. The result is a tremendous increase in the ratio of the heavy to light species.

One method of varying the energy in the seeded beam is to alter the number of heavy molecules in the beam, keeping the nozzle temperature unchanged. In the case of this research, this was accomplished by varying the temperature of the Mercury reservoir, and as a result, varying the Mercury vapor pressure. An alternative approach that was not
taken in this research is to combine carrier gases (Ar and Kr for instance). For this work, such a combination would be strategically unwise, as there would be a substantial increase in the types of clusters produced, making spectroscopic identification of specific clusters unnecessarily difficult. Furthermore, using single carrier gases separately allowed for the initial identification of the Mercury trimer.

Another method of beam energy variation is to keep the gas mixture constant (i.e. no change in carrier pressure or seed vapor pressure) and vary the nozzle temperature. For this method, care must be exercised not to exceed the maximum operating temperature of the valve.

Increasing the carrier gas pressure decreases the number of collisions between Mercury molecules, which reduces the number of clusters which do not contain at least one Argon atom.

If the carrier gas partial pressure is relatively high, it becomes possible to create clusters in which a seed atom is "encased" in carrier atoms (molecules). This would be the strategy for producing clusters such as HgAr\(^n\) (n > 1). For the production of Hg\(_n\)Ar (n > 1), the carrier gas partial pressure must be lower, accompanied by an increase in seed vapor pressure. It was this technique by which Hg\(_2\)Ar was produced for this research. Not surprisingly, the Argon partial pressure and Mercury vapor pressure are both higher for the production of Hg\(_2\)Ar, than for HgAr.

There has been a lot of study conducted in order to find a general scaling law for cluster size in a supersonic beam. For n > 10, the cluster density scaled approximately with the inlet pressure to the n\(^{th}\) power. However, effective nozzle size and geometry, and beam temperature are also very important factors in determining cluster size.
In the event that there is a large difference in the condensation energy between the carrier and the seed, clustering occurs primarily due to collisions involving the seed. Solvation clusters do not generally exist for long. Therefore, a heavy carrier (and thus a slow beam) allows for the formation of larger pure clusters due to a greater number of collisions prior to the termination of the beam expansion. Argon was selected for this research because it is highly efficient at removing condensation energy through collisions, and as a result, producing "studieable" amounts of Hg₃.

In order to cool the clusters within a supersonic molecular beam, two microscopic methods are available. Collisional cooling involves two-body collisions between seed and/or carrier molecules. Evaporative cooling occurs when large metastable clusters dissociate, and continues even into the collision-free region of the beam.

Van der Waals clusters are highly susceptible to the loss of surface atoms, and are thus metastable at all temperatures possible in a supersonic beam. Rotational temperatures are approximately 5-10 K; translational temperatures are approximately 1-5 K. Vibrational temperatures are generally 10 to 100 times larger than rotational temperatures.

As early as 1909 [22], it was predicted that a substance's melting temperature increased with an increase in the size of its constituent particles. Experimentally, this was verified in 1981 [23]. Useful for defining a cluster's melting point is the Lindemann criterion applied to clusters: if the average internuclear separation\footnote{Often called the bond length. The variation in nuclear separation can be represented by \((<r> - <r>^2)^{1/2}\) (the standard deviation), assuming that all values of \(r\) (the internuclear separation) are equally probable.} fluctuates by an amount \(\geq 10\%\), the structure will change and the cluster will melt.
It is generally assumed that the term structure (when applied to molecules) infers that the interatomic bonds are rigid and stable. This inference makes its application to small clusters difficult, as their geometries tend to fluctuate. For instance, Li$_3$, the simplest of all metal clusters, well illustrates this geometric complexity. Its electronic ground state is split into two nondegenerate states, as the result of an e × E Jahn-Teller effect. It has been determined that there are three distinct geometries within a 15meV range of the vibrationless ground state [24].

To determine the structure of more complex metal clusters including Hg$_3$ and Hg$_2$Ar, it would be necessary to perform detailed rotational and rotational-vibrational spectroscopic studies. Thus far, these studies have not been undertaken.
1.3 Laser-Molecule Interaction

In the case of a Gaussian cross-section laser beam propagating in the direction of +x in Cartesian space, with the beam waist\(^2\) located at the origin at \(t = 0\), the time and spatially dependent electric field is given by [25]:

\[
\vec{E}(x, y, z, t) = \vec{E}_0(x) \exp\left(-\frac{y^2 + z^2}{w^2}\right) \exp\left(\frac{ik(y^2 + z^2)}{2R}\right) \exp(i(kx - \omega t))
\]  

(1.6)

where \(k\) is the wave vector \((2\pi/\lambda)\), \(E_0(x)\) is the electric field amplitude along the x-axis, \(\omega\) is the angular frequency of the laser, \(w(x)\) is the 1/e radius of the electric field at any \(x\), and \(R(x)\) is the radius of curvature of the wavefronts at any \(x\).

If a molecule travelling at velocity \(u\) parallel to the z-axis encounters this laser, it will experience a time dependent-electric field. This is due to its motion, as well as encountering different amplitudes of the radiation that it traverses. In this instance, the electric field can be written as:

\[
\vec{E}(x, y, z, ut) = \left\{ \vec{E}_0(x) \exp\left(-\frac{y^2}{w^2}\right) \exp\left(\frac{iky^2}{2R}\right) \exp(iku) \right\} \left\{ \exp\left[ -\left(\frac{1}{w^2} - \frac{ik}{2R}\right)u^2t^2 \right] \exp(-i\omega t) \right\}
\]  

(1.7)

---

\(^2\) The beam waist is the location along the beam axis where the cross-sectional area of the beam is a minimum. The positions of the beam waist depend on the laser design, and the lenses and mirrors which steer and focus the beam.
The two sets of brace brackets represent the spatially and temporally dependent portions of the electric field.

The laser’s linewidth is independent of x and y. As a result, all molecules in a beam with the same velocity, crossing the laser in the direction of x will have identical line shapes.

A molecule travelling along +z and traversing a plane wavefront with constant field amplitude would be expected to have a field frequency spectrum with zero linewidth (i.e. monochromatic). At the beam waist the wavefront is a plane but the Gaussian variation of the field as a function of distance from the axis (and hence as a function of time) produces a finite linewidth. The linewidth is due to transit time broadening. When the beam has diverged, the wavefronts are no longer plane and a linewidth results from the variation in phase of the field due to curvature of the wavefront in addition to the variation of field amplitude with distance from the axis.

In the case of an actual supersonic molecular beam, even if well collimated, there will be a small velocity component perpendicular to the beam axis. This will result in Doppler Broadening.

Both transit time broadening and Doppler broadening were not significant concerns in this research because the spectral resolving power of the observation equipment was not sufficient to detect these weak effects. Furthermore, the molecular beam did not traverse the laser at the beam waist. This slight off-focussing was necessary to make as large as possible the excited volume of the molecular beam, while still maintaining an intense incident electric field.
Chapter 2

Theory
2 Theory

2.1 Introduction

Many clusters that are formed in supersonic expansion beams are weakly bound. Their constituent atoms are held together by the van der Waals interaction. The ground states of van der Waals molecules are particularly weakly bound, and as a result, clusters in their ground state dissociate easily from collisions. The supersonic beam offers a unique environment in which collisions are minimized, and clusters in the ground state become stable.

In the case of clusters containing a rare gas molecule, the rare gas atom-atom interaction is fitted by the Lennard-Jones potential, \( V_{L-J} \)

\[
V_{L-J} = \varepsilon \left[ \left( \frac{R}{R_o} \right)^{-12} - 2 \left( \frac{R}{R_o} \right)^{-6} \right] \tag{2.1}
\]

where \( \varepsilon \) is the potential well depth measured at \( R = R_o \) (the well minimum), and \( R_o \) is the internuclear separation at the well minimum.

The \( R^{-12} \) term, although too steep, models the repulsion between atoms caused by the filled orbitals. The \( R^{-6} \) term models the induced dipole – induced dipole interaction.

An alternative and more accurate choice of potential is the Morse potential

\[
V(R) = D \left[ 1 - e^{-\beta (R-R_o)} \right]^2 \tag{2.2}
\]

where \( D \) is the dissociation energy (potential for infinite nuclear separation), and \( \beta \) is the Morse parameter in cm\(^{-1}\).
The Morse potential represents the true potential quite well near the potential minimum, while the L-J potential is a good representation at large R near the dissociation limit.

Binding energies vary, but are generally approximately 10 meV range for neutral rare gas atoms [26]. The well depths for excited dimers and trimers are often much greater (0.5 eV to 1.0 eV). This is much less than the excitation energy of the atoms or the separation of the potential minima associated with different electronic molecular states which (typically 5 eV to 20 eV).

Since electronic transitions occur in a very short time, the nuclei “stand still” during this time. As a result, electronic and nuclear motions are separable, making valid the Born-Oppenheimer approximation and the Franck-Condon principle.

The electronic and vibrational structure of some triatomic molecules can be readily studied by means of laser fluorescence. It is much more difficult to resolve molecular structure to rotational resolution, and was not done in this research. The line width of a pulsed dye laser is wider than the rotational line spacing for the low rotational quantum numbers which occur in the molecular beam. In addition, Hg₂Ar and Hg₃ have large moments of inertia, resulting in large rotational constants, and thus, rotational spectral features that are very closely spaced spectrally. Therefore, only electronic and vibrational spectral theory is discussed.
2.2 Vibrational Motion of Trimers

2.2.1 Classical Mechanical Description

The motion of a triatomic molecule (see Figure 2.1) can be described classically with the Lagrangian formalism, \( L = T - V \). The kinetic energy \( T \) of the molecule may be written in Cartesian Coordinates as:

\[
T = \frac{1}{2} \sum_{j=1}^{3} m_j (\dot{x}_j^2 + \dot{y}_j^2 + \dot{z}_j^2)
\]  

(2.3)

where \( \dot{x}_j = \frac{dx_j}{dt} \).

It is very useful to introduce 9 mass-weighted coordinates, \( q_j \), defined as follows.

\[
q_1 = \sqrt{m_1} (x_1 - x_{1e})
\]

\[
q_2 = \sqrt{m_1} (y_1 - y_{1e})
\]

\[
q_3 = \sqrt{m_1} (z_1 - z_{1e})
\]

\[
q_4 = \sqrt{m_2} (x_2 - x_{2e})
\]

\[
q_5 = \sqrt{m_2} (y_2 - y_{2e})
\]

\[
q_6 = \sqrt{m_2} (z_2 - z_{2e})
\]

\[
q_7 = \sqrt{m_3} (x_3 - x_{3e})
\]

\[
q_8 = \sqrt{m_3} (y_3 - y_{3e})
\]

\[
q_9 = \sqrt{m_3} (z_3 - z_{3e})
\]

(2.4)

Where \( x_{1e} \) is the equilibrium position of atom 1, etc.

(2.3) can now be simplified to (2.5).

\[
T = \frac{1}{2} \sum_{j=1}^{9} \dot{q}_j^2
\]  

(2.5)
The coordinates \( q_i \) specify the location of the nuclei relative to the equilibrium position at the global minimum of potential energy. The potential energy \( V(r) \) can be written in a Taylor expansion about \( q_i = 0 \). If it is assumed that the expansion is taken to be a harmonic potential, then as a result, it is truncated after the second order term.

Furthermore, \( \frac{\partial V(r)}{\partial q_j} \bigg|_{q_i = 0} = 0 \) The potential energy has a local minimum value at the equilibrium position. Force constants \( f_{jk} \) are defined by the second derivatives of the potential as follows.

\[
f_{jk} = \left. \frac{\partial^2 V}{\partial q_j \partial q_k} \right|_{q_i = 0}
\] (2.6)

Using the generalized coordinates \( q_i \), the Langrangian can be written explicitly (2.7).

When inserted into Lagrange's equation (2.8), the result is a set of 9 coupled second-order ordinary differential equations with constant coefficients.

\[
L = \frac{1}{2} \sum_{j=1}^{9} \dot{q}_j^2 - \frac{1}{2} \sum_{j=1}^{9} \sum_{k=1}^{9} f_{jk} q_j q_k
\] (2.7)

\[
\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_j} \right)_{q_i} = \left( \frac{\partial L}{\partial q_j} \right)_{q_i}, \quad j = 1, ..., 9
\] (2.8)

If a solution of the form (2.9) is assumed, the resulting \( 9 \times 9 \) determinant (2.10) must equal zero to avoid a trivial solution to the 9 equations.

\[
q_j = C_j \cos(\sqrt{\gamma} t + \theta)
\] (2.9)

\[
\begin{vmatrix}
  f_{11} - \gamma & f_{12} & \cdots & f_{19} \\
  f_{21} & f_{22} - \gamma & \cdots & \vdots \\
  \vdots & \ddots & \ddots & \vdots \\
  f_{91} & \cdots & \cdots & f_{99} - \gamma
\end{vmatrix} = 0
\] (2.10)
Of the 9 values of $\gamma$ (the eigenvalues of the force constant tensor), six are zero for a non-linear molecule, and 5 are zero for a linear molecule. There are three degrees of freedom for translation, two for the rotation of a linear molecule (three for a non-linear molecule).

It is useful to introduce the normal mode coordinate, $Q_m$, defined by

$$Q_m = \sum_k l_{mk} q_k$$  \hspace{1cm}  (2.11)

where $l_{mk}$ are the elements of the linear coordinate transformation matrix which arises from diagonalising the force constant matrix.

The potential can now be rewritten in terms of the normal mode coordinates

$$V = \frac{1}{2} \sum_j \gamma_j Q_j^2$$  \hspace{1cm}  (2.12)

The three non-zero values of $\gamma$ are the frequencies of the three completely independent oscillators. In reality however, this is not strictly true. A real molecule would be described by an expansion of the potential that would contain higher order terms.

2.2.2 Quantum Mechanical Description

The generalized momentum can be easily written in terms of the normal mode coordinates.

$$P_j = \left( \frac{\partial L}{\partial \dot{Q}_j} \right)_{Q_i} = \dot{Q}_j$$  \hspace{1cm}  (2.13)
Using the typical definition of the momentum operator \( \hat{p}_j = -i\hbar \frac{\partial}{\partial \hat{q}_j} \), the Hamiltonian operator, \( \hat{H} \), is given by (2.14).

\[
\hat{H} = \frac{1}{2} \sum_j \left[ \gamma_j \hat{\omega}_j^2 + \hbar^2 \frac{\partial^2}{\partial \hat{q}_j^2} \right]
\]  

(2.14)

Thus, the solution to the Schrödinger equation \( \hat{H}\varphi = E\varphi \) is the product of 3 (or 4 for a linear molecule) wavefunctions of the harmonic oscillator.

\[
\varphi = \prod_{j=1}^3 \varphi_j(\hat{q}_j)
\]

(2.15)

The total vibrational energy of the molecule is just the sum of the energies of the individual oscillators.

\[
E = \sum_{j=1}^3 \hbar \sqrt{\gamma} \left( \nu_j + \frac{1}{2} \right)
\]

(2.16)

This approach makes the assumption that the molecule does not rotate. Although real molecules do rotate, their vibrational motion is reasonably well described by (2.16). Furthermore, real molecules are anharmonic oscillators, in which the anharmonicity can be considered a combination of the zeroth-order wavefunctions of the harmonic oscillator [27].

Rotational and vibrational motions are not separable. If the coordinate system of the molecule is noninertial, then a Coriolis force is introduced. The classical Hamiltonian must then be transformed into its quantum mechanical counterpart taking into account the additional Coriolis terms. It is these terms that mix the vibrational and rotational wavefunctions. Even so, the purely vibrational model is particularly successful.
2.2.3 Normal Modes and Structure

Normal modes of vibration occur when the coordinates of each atom in a molecule vibrate both in phase with each other, and at the same frequency. Figure 2.2 shows the normal modes possible in a non-linear trimer.

It is expected that Hg$_2$Ar and Hg$_3$ are both non-linear molecules, and thus triangular. Martrenchard-Barra et. al. [28] have resolved the structure of HgAr$_n$ (n $\geq$ 2) and found HgAr$_2$ to be T-shaped in the ground state. The bond common to both Hg$_2$Ar and HgAr$_2$ is obviously Hg-Ar, with a binding energy of 130 cm$^{-1}$ [29]. The binding energy of Hg-Hg and Ar-Ar are 380 cm$^{-1}$ [30] and 395 cm$^{-1}$ (calculated at 298 K) respectively [31]. This difference in binding energies indicates that the triangular shape of Hg$_2$Ar is not equilateral. However, Hg$_3$ is most likely shaped like an equilateral triangle, as all binding energies are 380 cm$^{-1}$.

2.2.4 Vibrational Selection Rules

The following is the vibrational wavefunction for the ground state of a triatomic molecule.

$$\psi_0 = \prod_{j=1}^{3} \phi_0(\xi_j)$$

(2.17)

where $\xi_j = Q_j \sqrt{\frac{\omega_j}{\hbar}}$

Consider the excitation of the $j^{th}$ vibrational mode by a single photon, in which case $\psi(v_j = 1)$ replaces $\psi(v_j = 0)$. In this event, (2.17) becomes:

$$\psi_1 = \phi_0(\xi_1)\cdots\phi_1(\xi_j)\cdots\phi_0(\xi_3)$$

(2.18)
The intensity of a vibrational mode is given by

\[ I_{f\rightarrow i} \propto \left| \left( \frac{\partial \mu}{\partial Q_k} \right)_0 \int \phi_i(\xi_i) Q_k \phi_0(\xi_k) dQ_k \right|^2 \]  \hspace{1cm} (2.19)

where \( \mu \) is the dipole moment.

The above integral is the \textit{transition moment} integral. This integration is done over the initial and final vibrational wavefunctions (\( \psi_i, \psi_f \)) in the same electronic state. However, \( \psi_i \) and \( \psi_f \) can be expanded in terms of the wavefunctions of the individual atoms, as shown in (2.16). The dipole moment \( \mu \) can be expanded in a Taylor series (2.20).

\[ M = \mu_0 \int \phi_f^* \phi_i dQ + \sum_{l=1}^{3} \left( \frac{\partial \mu}{\partial Q_l} \right)_0 \int \phi_f^* Q_l \phi_i dQ + \cdots \]  \hspace{1cm} (2.20)

All higher order terms have been neglected. The first term is zero, and in the sum, only the \( l^{th} \) term survives because \( \psi_i \) and \( \psi_f \) are given by Hermite polynomials, which are mutually orthogonal.

Only a change in the vibrational quantum number of a single vibrational mode will allow a transition (i.e. \( I_{f\rightarrow i} \neq 0 \)). The selection rule \( \Delta \nu = \pm 1 \) applies only to pure vibrational transitions in harmonic oscillator potential wells.

If the molecules in the beam were to be in thermal equilibrium, the Boltzmann distribution law gives the ratio of the number of molecules in an excited state to the number of molecules in the ground state.

\[ \frac{N}{N_o} = \exp \left( -\frac{\nu}{0.69527} \right) \]  \hspace{1cm} (2.21)
where \( N, N_0 \) are the numbers of molecules in the excited and ground states respectively, \( \nu \) is the frequency of the excited vibration in cm\(^{-1}\), and \( T \) is the absolute temperature.

In a cold beam, the number of molecules in the ground state is much higher than if the molecules were hot, for any given frequency of vibration. Thus, the clear advantage of a supersonic expansion over molecular vapor contained in a cell is in the investigation of ground state van der Waals clusters.

### 2.4 Electronic Spectroscopy of Trimers

#### 2.4.1 Molecular Orbitals

In order to study the electronic structure of trimers, it is necessary to consider the electronic Schrödinger equation.

\[
\hat{H}_{el} \phi = E_{el} \phi \tag{2.22}
\]

A useful solution to this equation is a set of molecular orbital wavefunctions comprised of a linear combination of the three atomic orbital wavefunctions.

\[
\phi_{mol} = \sum_{j=1}^{3} c_j \phi_j \tag{2.23}
\]

The total molecular orbital wavefunction is the Slater determinant of the individual molecular orbital wavefunctions [32].

\[
\phi = |\phi_{mol} (1) \phi_{mol} (2) \cdots | \tag{2.24}
\]

There exists a group of symmetry operators \( \{O_R\} \), which have these electronic molecular orbital wavefunctions as eigenvalues, and which commutes with the electronic Hamiltonian, \( \hat{H}_{el} \).
\[ [\hat{O}_r, \hat{H}_{el}] = 0 \]  

(2.25)

2.4.2 Vibrational Selection Rules in Electronic Transitions

The vibrational selection rules in electronic transitions are determined from the Franck-Condon principle\(^1\). The transition moment integral \(M_{e'v'}\) is given by

\[
M_{e'v'} = M_{e,v'} \int \varphi_{v'}^* \varphi_{v'} dQ_1 \int \varphi_{v'}^* \varphi_{v'} dQ_2 \int \varphi_{v'}^* \varphi_{v'} dQ_3
\]

(2.26)

This transition moment integral is for a non-linear trimer, and is valid under the normal mode approximation and the Born-Oppenheimer approximation. A linear trimer would contain an additional overlapping integral (ie. \(3N - 5\) normal modes). The term \(M_{e'v'}\) is the electronic transition dipole moment \(\int \varphi_{e'}^* \mu_e \varphi_{e'} d\tau_{el}\).

For totally symmetric vibrations, the selection rule for allowed frequencies is: \(\Delta v_i = 0, \pm 1, \pm 2\ldots\) The Franck-Condon factor (2.27) determines the transition intensity.

\[
\left| \int \varphi_{v'}^* \varphi_{v'} dQ_i \right|^2
\]

(2.27)

However, if the vibrations are not totally symmetric, then \(\left| \int \varphi_{v'}^* \varphi_{v'} dQ_i \right|^2 = 0\) for \(\Delta v_i = \pm 1, \pm 3, \pm 5\ldots[33]\). For nonsymmetric vibrations during a permitted electronic transition, the selection rule is: \(\Delta v_i = \pm 2, \pm 4, \pm 6\ldots\)

\(^1\) Classically, the Franck-Condon principle states that transitions can occur only vertically on a potential energy, nuclear separation diagram.

This is reasonable since electronic transitions occur in less than \(10^{-15}\) s, and thus approximately, the nuclei do not move in this time.
2.5 Nonradiative Transitions

Part of the challenge facing the investigation of a new molecular species is being certain that the species actually radiates when a transition occurs from a higher state to a lower state. However, absorbed energy can be dissipated by means of intramolecular interactions. Electronic energy can be converted into vibrational energy in the absence of collisions.

However, this is most often the case with large molecules. For small molecules, the lack of fluorescence following laser excitation is most often due to collisional transfer to other states, or due to dissociation of the molecule.
Figure 2.1. A triatomic molecule shown in the Cartesian coordinate system.
Figure 2.2. Normal modes of vibration for Hg$_2$Ar and Hg$_3$. 
Chapter 3

Apparatus Description
3 Apparatus Description

3.1 The Laser System

The system used for molecular excitation was a $\text{N}_2$ pumped tuneable dye laser. Alignment of the system was highly critical to ensure that the maximum possible $\text{N}_2$ energy was absorbed by the dye.

The dye laser consisted of oscillator and amplifier sections (see Figure 3.1). The Coumarin 500 dye was held in UV transparent, model 509 Princeton Cells, Inc. cuvettes. The output of the dye laser was doubled using a BBO - ‘C’ doubling crystal. The second harmonic was linearly polarized, and a prism spatially separated it from the fundamental over a distance of approximately 35 cm. The second harmonic was passed through a second prism that was oriented at $180^\circ$ with respect to the first prism, before being reflected toward the vacuum chamber by a UV reflecting mirror. This second prism served to reduce the amount of beam travel when the wavelength of the dye laser was changed (see Figures 3.2a and 3.2b). See Appendix 1 for more detail on laser frequency doubling.

The Nitrogen laser radiation was directed into the dye laser by means of two reflecting mirrors. The first mirror reflected 25% of the incoming UV to the oscillator section. The remaining 75% was reflected by a 100% reflecting mirror into the amplifier section. Two 5 cm cylindrical quartz lenses focussed the beams onto the dye cuvettes. The excited volume of dye was approximately $8 \text{ mm} \times 2 \text{ mm} \times 1 \text{ mm} = 16 \text{ mm}^3$ [34]. The total volume held by the cells was 3 cm$^3$, and was magnetically stirred. The useful lifetime of the dye at 10pps varied, but tended to average approximately 7 hours.
The dye, supplied by Exciton, produced maximum laser output at the desired wavelength when prepared at a concentration of 0.01 moles/liter using ethanol as a solvent in the oscillator stage. The concentration was halved in the amplifier stage. The Coumarin 500 dye was chosen as its second harmonic covers a lasing range from 2365 Å to 2735 Å, although lasing at these limits was found to be very weak. The wavelength of maximum fluorescence was found to be approximately 5000 Å (2500 Å for the second harmonic).

The dye laser wavelength was adjusted by means of a stepping motor connected by a micrometer screw to a Bausch and Lomb diffraction grating with a 54° blaze angle and a groove density of 600 mm⁻¹ in a Littrow mounting. A homemade beam expander was used to spatially expand the incident N₂ laser radiation across the full width of the grating. The smallest increment of the stepper motor moved the grating by an angle that corresponded to a frequency change of 0.3 cm⁻¹ at 2500 Å.

3.1.1 Dye Laser Calibration

The angle of incidence of the fundamental laser wavelength on the BBO – ‘C’ crystal was determined by the phase matching condition and varied with wavelength. Therefore, the crystal angle needed to be adjusted as the grating angle changed. To accomplish this, a microcomputer was used to control both the grating stepping motor, and the stepping motor connected to the crystal’s rotating mount by a precision screw thread.
A calibration was done, and the relationship between the grating and doubling crystal steps is given by

\[ S_D = 1.27929S_G - 0.0001228S_G^2 \]  (3.1)

where \( S_D \) and \( S_G \) are the number of steps of the doubling crystal and grating motors respectively.

Although the contribution of the quadratic term appears small, it becomes significant for wavelength changes greater than several angstroms.

### 3.2 The Vacuum/Heating Systems

The frequency doubled dye laser radiation intersected the molecular beam in a 26 cm diameter vacuum chamber. The chamber was evacuated by a Roots pump connected to an Edwards Model E2M-80 roughing pump to achieve a pressure of approximately \( 5 \times 10^{-3} \) torr, and was measured with an Edwards Thermocouple 507 manometer. This pressure resulted in a mean free path of approximately 3.5 cm.

A 0.45 cm in diameter stainless steel tube was fed through the chamber and connected to a General Valves Series 9 high temperature pulse valve, capable of being heated to 235°C. Connected to the valve was a homemade nozzle. The nozzles were made from stainless steel, and were blackened with liquid graphite to reduce stray light. The nozzle diameters ranged from 60 \( \mu \)m to 900 \( \mu \)m. The valve assembly was covered with an electric heating coil, which fitted snugly inside a blackened ceramic cover. The front of the nozzle was located at the center of the chamber.

The laser and valve were triggered with a homemade pulse generator. An optimum delay of 417.3 \( \mu \)s (within approximately 1 \( \mu \)s) between the laser and valve
pulses was needed, and was accomplished with a Berkeley Nucleonics Corporation Model 7010 Digital Delay Generator. The time taken by the laser beam to traverse the total distance to the chamber was approximately 13 ns, and thus was inconsequential to the setting of the delay generator.

The repetition rate of the valve and laser was 10 Hz, and the valve pulses had a duration of 2 ms. A pulsed valve was chosen to avoid unnecessary use of both Mercury and the carrier gas, as well as allowing the pumps to maintain a lower chamber pressure. The laser beam was reflected off a 2.5 cm mirror mounted above the chamber, and was focussed by a 5 cm diameter double convex quartz lens. The beam entered the chamber through the center of a 7.5 cm diameter quartz window, and was targeted between 5 mm and 25 mm in front of the nozzle, and perpendicular to the molecular beam. This target distance is well within the 35 mm mean free path. The laser spot size was approximately 1 mm. A variable aperture was used to help minimize the scattered light that entered the chamber, and was placed on the quartz window. The typical aperture diameter was 2.5 mm.

The stainless steel tube was connected to a hose that ran to a bottle of compressed inert gas. This carrier gas was brought into the chamber under pressure that varied from 0.17 atm to 10.2 atm. Located beneath the tube and outside of the chamber was a reservoir containing liquid Mercury. The reservoir was electrically heated to obtain vapor pressures between 8 and 450 torr. The stainless steel tube and inlet to the chamber were also electrically heated. The vapor from the reservoir was forced through the pulse valve by the inert gas and into the chamber supersonically. Clusters were formed by collisional processes within the supersonic expansion.
The temperatures of the valve, inlet, nozzle, and tube were controlled individually by rheostats, and measured with thermocouples. The voltage of the thermocouples was measured with a digital voltmeter, and related to the temperature through a calibration curve. The maximum temperature rating of 235°C corresponds to a thermocouple voltage of 10.5 mV.

3.3 The Data Collection System

3.3.1 Excitation Spectrum: Conventional Spectroscopy

The fluorescence light from the supersonic beam was monitored along a direction mutually perpendicular to both the laser beam and to the molecular beam. The fluorescence was collected by a 5 cm diameter fused quartz lens, and was focused onto the photocathode of an EMI Gencom Inc. Model FACT 50 Photomultiplier. The photomultiplier was air cooled with a Model FACT 50 MKII cooler. An Ortec Model 456 High Voltage Power Supply provided the 1500 V – 2500 V needed for the photomultiplier.

A Hewlet Packard Model HP5411D digitizing oscilloscope was connected to the photomultiplier, and to a microcomputer. The data collection software was specially written to operate with the Hewlet Packard controller card in the microcomputer, and with the Hewlet Packard hard drive partition.

A stray fundamental beam from the laser was sent to a photodiode whose output triggered the digitizing oscilloscope. The oscilloscope has a built-in delay function to set the start of the digitizing pulse relative to the trigger pulse. The delay was typically 10
ns, the duration of the laser pulse, and it eliminated the strong scattered dye laser light signal from the fluorescence signal.

Since the total fluorescence was collected by the “wavelength blind” photomultiplier, it was necessary to reduce the scattered light within the chamber as much as possible. This was accomplished with a blackened plastic beam trap placed on the chamber bottom beneath the laser pulse, by blackening the inside of the chamber, and a blackened aluminum “light tunnel” between the excitation point and the chamber exit window. In addition, black cloths were placed around the external lens and photomultiplier to further reduce the scattered light. Covering the dye laser with a cardboard shield helped noticeably in reducing stray light from the oscillator and amplifier cuvettes.

The “light tunnel” was perpendicular to the molecular beam in order to greatly reduce doppler broadening of the emitted fluorescence.

3.3.2 Excitation Spectrum: Charge-Coupled Device Camera

In addition, a Princeton Instruments Model TCCD-1024MLOG-H1 CCD camera was used to observe excitation spectra. The camera was cooled with cold water flowing at 1.76 L/min. Nitrogen gas flowed through the camera at the rate of 400 cm$^3$/min, and was used to flush away any water vapor that might condense on the camera optics.

The CCD camera contained an EEV 1024 × 256 pixel array sensitive from below 2000 Å to beyond 10,000 Å. It was placed in the exit plane of an ISA Instruments HR320 monochromator which spatially spread the fluorescence across the pixel array. The monochromator, which served as a spectrograph, was equipped with a plane
1800 mm\(^{-1}\) diffraction grating, and used 0.32 m spherical mirrors in a Czerny-Turner arrangement. The dispersion of the fluorescence on the pixel array was dependent on both the central wavelength at which the monochromator was set, as well as the grating parameters and the focal length of the exit mirror in the monochromator. When centered at 2500 Å, it was found to be 2.526 pixels/Å (6.25 cm\(^{-1}\)/Pixel) for the ISA Instruments HR 320 and a wavelength range of approximately 2300 Å to 2700 Å could be observed.

The camera output was connected to a microcomputer, which collected, stored, and displayed the accumulated spectra. In addition, the computer controlled all laser and spectrometer motions. The programs used to control the laser and spectrometer settings, as well as the data collection from the CCD camera were both supplied by Princeton Instruments Inc., and specially written in Spectrum Basic®.

To accumulate an excitation spectrum, the spectrometer was set at 0 Å, and the total fluorescence, independent of wavelength, was accumulated on a single pixel column near the array center. This was repeated for each excitation wavelength of the laser.

The CCD camera system was less sensitive and required greater exposure times than the photomultiplier, thus requiring great care in reducing ambient scattered light.

3.3.3 Fluorescence Spectrum: Charge-Coupled Device Camera

The tremendous advantage in using the CCD camera is in obtaining a fluorescence spectrum. With a 400 Å view at 2500 Å, the camera obtains the fluorescence immediately, as it would obtain an excitation spectrum. The spectrometer was then stepped to examine fluorescence beyond the 400 Å view. These spectra could then be “stitched” together, forming a continuous spectrum across the desired range.
This is in stark contrast to a monochromator used in conjunction with a photomultiplier, in which the monochromator must be set at each fluorescence wavelength, and the data collected.
Figure 3.1. A two stage dye laser. The cuvettes are pumped transversely by the 337.1 nm output of a Nitrogen laser.
Figure 3.2a. Schematic of a tuneable dye laser system.
Figure 3.2b. Frequency doubling stage of tuneable dye laser. The second harmonic is separated from the fundamental by the first prism. The separated fundamental diverges from the second prism, clear of the UV mirror, and is not shown.
Chapter 4

Experimental Procedure
4 Experimental Procedure

4.1 Initializing the Data Collection System

Prior to vacuum chamber evacuation and laser alignment, the CCD camera system had to be started. This was necessary to align the laser to the target area of the molecular beam. For approximately five minutes, cold water and nitrogen flowed through the camera system, after which the temperature controller for the CCD camera was turned on, and the camera was allowed to reach its operating temperature.

Data collection could only begin in the dark, as ambient room light could destroy the pixel array. With the camera and spectrometer aligned, and the fluorescence focusing lens in place, the laser could then be targeted.

4.2 Targeting the Laser

The heated cathode of the nitrogen laser's thyratron was allowed to heat up for five minutes before the high voltage supply was turned on. The dye laser was adjusted for maximum operating efficiency, and the second harmonic was aligned with the reflecting mirror above the chamber.

A small Aluminum “targeting rod” was placed at the nozzle aperture. The laser pulse reflecting off the rod was observed with the CCD camera, and the reflecting mirror and lens were adjusted for maximum intensity\(^1\) (see Figure 4.1). UV sensitive paper allowed direct viewing of the laser spot. Final adjustments were also made on the

\(^1\) The Princeton Instruments program setting used to observe the laser pulse was “Locate Spectrum Position”.

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fluorescence focusing lens and spectrometer positions. The manual adjustment program
for the dye laser (see Appendix 4) was used to set the dye laser to the appropriate
wavelength, which was measured with the CCD camera. Once the laser was aligned, the
targeting rod removed, and the “light tube” and beam dump adjusted, the chamber lid was
put in place.

4.3 System Evacuation and Heating

The vacuum chamber was pumped down to a background pressure of $10^{-3}$ torr.
The heaters were turned on and adjusted to heat the valve, mercury reservoir, chamber
inlet, and carrier supply pipe to their operating temperatures. This evacuation and
heating process took approximately one hour. During this time, the nitrogen laser was
operating, but not lasing. The CCD controller was also left on, but no data collection
program was running.

The most critical temperature setting was that of the mercury reservoir, as this
determined the vapor pressure. During the experiment, it was this temperature that was
continuously monitored. The valve temperature was also quite important, and was not to
exceed 235°C for the General Valve Series 9. Occasionally, this temperature limit was
exceeded which resulted in temporary malfunctioning of the solenoid.

The inlet was heated to a slightly lower temperature than the valve, so as to
prevent condensation of the mercury vapor prior to being released into the chamber. The
pipes were heated to the lowest of all four temperatures, in order to prevent reverse
migration of the mercury vapor.
4.4 Data Collection

Once the chamber was evacuated and the temperatures of the valve and mercury reservoir were stable, the carrier gas valve was opened, and the nitrogen laser was set to external trigger. The pulse generator was started, which opened the valve and fired the laser in sequence.

The spectrum was then collected under the control of either the manual control program, or the automatic control program (see Appendix 3). Unlike the photomultiplier, there is no delay setting for the CCD camera. It collects the light continuously. The system has the capability of collecting only scattered light, and then subtracting that scan from the scan of the spectrum and scattered light. The result is a spectrum without scattered light.

The required exposure time was highly variable and was dependent upon the dye laser intensity, the spectrometer slit width and wavelength, and was on the order of several minutes. Extended exposures were attempted, but the CCD camera was overloaded with ambient light, and no spectra were observed².

4.5 CCD Camera Wavelength Calibration

In order to interpret a spectrum on the CCD pixel array, the wavelength as a function of pixel number needed to be determined. A mercury lamp was placed in the entrance plane of the spectrometer, established spectral lines observed, and a calibration was done.

² As the light collected by the CCD camera accumulated, intensity from one column could tend to "smear" upon neighbouring columns, and obscure detail.
The monochromator was set at 2536 Å. The observed Hg spectral lines were located at 2536.52 Å, 2563.86 Å, and 2576.29 Å. The corresponding pixels at which these lines were observed were 537, 606, and 637 respectively.

Applying a least squares fit to this data resulted in a dispersion of $2.526 \pm 0.005$ Pixels/Å ($6.15 \pm 0.01 \text{ cm}^{-1}/\text{Pixel}$). The corresponding observed spectral range was $405.7 \pm 0.6$ Å.

A spectral feature with a wavelength identical to the spectrometer wavelength setting will appear at pixel $537^3$. Therefore, a spectrometer setting of 2500.0 Å would result in spectral coverage from 2287.2 Å to 2692.8 Å.

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$^3$ This pixel number was dependent (within 5%) upon the angle of the pixel columns with respect to the monochromator's exit plane. Occasional calibration checks with a mercury lamp were necessary to ensure the camera remained properly positioned.
Figure 4.1. Partial schematic diagram of the vacuum and data collection systems showing the placement of the laser targeting rod. The laser enters the chamber perpendicular to the page.
Chapter 5

Results and Discussion
5 Results and Discussion

5.1 Introduction

Excitation and fluorescence spectra of several new species in a supersonic expansion beam were examined. There is strong evidence to support the conclusion that these species are Hg$_2$Ar and Hg$_3$. To produce the excitation spectra, the laser was scanned from 2525 Å to 2550 Å. The fluorescence was examined from 2000 Å to 8000 Å. The minimum spectrometer slit width corresponded to a monochromator linewidth of 8 cm$^{-1}$. Smaller widths reduced the intensity, and the signal vanished.

Data was collected with a Princeton Instruments CCD camera system. This data was downloaded into ASCII files, and averaged over all 256 pixel rows of the array. Scattered light was also collected, and this was subtracted from the accumulated spectra. Great care was exercised in not eliminating spectral structure during this subtraction process. Smoothing of the data was accomplished by calculating the mean of the intensities of neighboring pixels.

The excitation spectra presented here are verifications of work already presented in the literature. All fluorescence spectra discussed here are previously unobserved, and provide an extension of work already published.

5.2 The Excitation Spectra

This is verification of work done by Koperski, Atkinson, and Krause [14]. These excitation spectra were produced when the laser was scanned from 2525 Å to 2550 Å. By setting the HR 320 spectrometer to 0 Å, the total fluorescence was accumulated. A UV transmitting filter with an effective range of $\lambda < 3000$ Å was used to help reduce the
scattered light reaching the CCD array. The spectra were produced with two argon
carrier gas pressures and mercury vapor pressures. Figures 5.1 and 5.2 show these
spectra. Table 5.1 is a tentative assignment of spectral features [14].

Several well established excitation peaks in this vicinity serve as "wavelength
markers" to help identify the wavelengths of new features. The Hg2 0′s(63 P) ← X0′s
and HgAr A0+ ← X0+ and B1 ← X0+ transitions are particularly useful for this.

For 33 ≤ x/D ≤ 67 and 1 ≤ P_{Ar} ≤ 3 atm, very faint structures appear between
2525 Å and 2530 Å, and again between 2540 Å and 2545 Å. These have been attributed
to vibrational components of HgAr2 [35, 36]. As the argon pressure increases, HgAr_m (m
> 1) complexes increase in number [3, 4], and the B ← X transitions appear on the short
wavelength side of the HgAr B1 ← X0+ band [3, 4]. These peaks are not visible in either
Figure 5.1 or 5.2, because the x/D and P_{Ar} ranges are different.

When the carrier gas pressure is increased, as in Figure 5.2, the two strongest
peaks on the short wavelength side of the atomic line become more pronounced. These
peaks overlap the already well established peaks of the HgAr B1 ← X0+ transitions. The
fluorescence arising from the excitation of the two strongest peaks on the short
wavelength side of the atomic line has vibronic structures, which are examined in later
sections. In the range of 2525 Å to 2530 Å, the continuum is due to the dissociation of
the HgAr B1 state.

Koperski et. al. [14] found that when a continuous supersonic expansion beam is
used with a much higher Hg vapor pressure, the HgAr B1 ← X0+ transitions disappear,
and the A0+ ← X0+ transitions are present only for high carrier gas pressures. It was
observed when the Hg vapor density and argon pressure increase, the intensities of the
new complexes increase. Furthermore, the intensity of the Hg$_2$ $0^+_v\left(6^3P_1\right)\leftarrow X0^+_g$ band also increases. It is therefore reasonable that the production of the new complexes on the short wavelength side of the atomic line, logically believed to be Hg$_2$Ar, is strongly dependent on collisions between Hg$_2$ and an argon atom within the supersonic beam.

Koperski et. al. [14] repeated these spectral runs using krypton as the carrier gas. Complexes identified as HgKr undergoing B1 $\leftarrow$ X0$^+$ and A0$^+$ $\leftarrow$ X0$^+$ vibronic transitions, as well as Hg$_2$ undergoing $0^+_v\left(6^3P_1\right)$ $\leftarrow$ X0$^+_g$ were present at low krypton pressures. The new features that appeared on the short wavelength side of the atomic line with argon, were absent with krypton, and vice versa. This strongly suggests that these features were indeed due to Hg$_2$Ar.

However, a single feature on the long wavelength side of the atomic line, located at 2537.2 Å, occurred in both argon and krypton experiment runs, making it very likely that this new feature is due to Hg$_3$.

5.3 The Fluorescence Spectra

The fluorescence of five peaks (2534.3 Å, 2534.6 Å, 2535.8 Å, 2536.0 Å, 2537.2 Å) and one “valley” (2533.7 Å), which appear in the excitation spectrum in Figure 5.2, were observed. The region from 2000 Å to 8000 Å was examined, and the only fluorescence detected was in the vicinity of the peaks themselves. Koperski et. al. [14] also reported that all fluorescence from all peaks of Hg$_2$Ar or Hg$_3$ excited in the vicinity of the atomic line occurred at wavelengths less than 3000 Å. In fact, all fluorescence of all peaks excited in this region was confined to the UV. That result is confirmed here.
It is fairly obvious that individual rotational lines cannot be resolved in either the absorption spectra or the fluorescence spectra. Only low J values will be populated in the cold molecular beam, and the rotational lines will be spaced by no more than 1 cm\(^{-1}\) which is well below the resolution of these experiments.

The lack of signal appearing in the IR eliminates the possibility of the molecules decayed to an excited electronic state. Rather, they decayed back to the ground state, or a state only just above it.

Observations of these spectra would be most unlikely in a fluorescence cell, since the molecules would dissociate if they were in an environment where many collisions occur continuously.

It was found that the delay between the opening of the pulsed valve and the laser pulse was important in probing the fluorescence of these peaks. By varying the valve-laser delay within the range of 3 ms to 7 ms, it was possible to probe different species within the beam. A relatively long delay was necessary to probe the fluorescence of these peaks. Short delays are useful for probing diatomic molecules such as Hg\(_2\) and HgAr. As the delay was reduced, the fluorescence vanished. This dependence on valve-laser delay is not surprising. Larger clusters almost certainly require additional time for more collisions to occur in order to form, before then being excited. Koperski et. al. [14] note that this effect is particularly prevalent for the Hg\(_2\)Ar 4040 Å band fluorescence, excited with 2056 Å laser radiation.
5.3.1 Fluorescence Spectrum of the 2534.3 Å Peak of Hg₂Ar

This fluorescence spectrum was of the weakest of the chosen peaks from the excitation spectrum, and is labelled peak 9 in figure 5.2. With a spectrometer slit width corresponding to 8 cm⁻¹, the spectrum was collected and is shown in Figure 5.3. The spectrum clearly shows five distinct peaks at approximately 1 Å spacing. The average spacing of these peaks is approximately 12.5 cm⁻¹. This is the spacing of the electronic ground state levels. The first and most intense of these peaks appears at 2534.3 Å. This appears to indicate that the molecule is undergoing transitions from an undesignated higher state to the ground state. The relative heights of the fluorescence peaks are determined by the Franck-Condon factors.

The five peaks seem to be part of a bound-bound spectrum. However, it appears as though there may be a structured continuum on the long wavelength side of the five peaks. If so, this continuum would indicate that the upper vibrational state can make transitions to the repulsive part of the lower state (i.e. bound-free spectrum). This suspected continuum does appear to stretch over a comparable spectral region to that observed in Figure 4 of the paper by Fuke et. al. [1].

Increasing carrier gas pressure from 3.4 atm to 6.8 atm increased the intensity of the fluorescence. Beyond 6.8 atm, there were no noticeable effects on the spectra. However, decreasing carrier gas pressure caused the spectrum to quickly vanish. This is likely because fewer collisions with argon atoms failed to produce Hg₂Ar.
5.3.2 Fluorescence Spectrum of the 2534.6 Å Peak of Hg₂Ar

This peak, labelled 10 in Figure 5.2, is considerably more intense in the excitation spectrum than is the 2534.3 Å peak. Its fluorescence spectrum is shown in Figure 5.4, and the wavelength assignment of peaks is in Table 5.3. Thirteen distinct peaks are visible in this fluorescence spectrum, and cover a range of approximately 11 Å. The average spacing of the first few peaks is 12.5 cm⁻¹, allowing for missing peaks. This is identical with the spacing observed for the 2534.3 Å peak.

Peaks 9 and 10 would appear to be between the same manifold of vibrational states in both the upper and lower electronic states. The 4.7 cm⁻¹ spacing between peaks 9 and 10 is smaller than expected unless the potential well of the upper state is extremely shallow. It is possible that 4.7 cm⁻¹ comes from the difference between 12.5 cm⁻¹ (lower spacing) and 7.8 cm⁻¹ or 17.2 cm⁻¹ for the upper level spacing.

Like the 2534.3 Å peak, there appears to be a bound-bound spectrum followed by a short structured continuum. In this fluorescence spectrum, the slower variation of the Franck-Condon factors for the different vibrational states gives rise to more fluorescent peaks. The spacing between peaks 1 and 2 is almost exactly double the spacing of the other peaks. This is probably due to an unresolved peak which can be seen on the long wavelength side of peak 1.

Varying the argon pressure had the same effect as for the previous peak. For carrier pressures approaching 10.2 atm, no improvement in the intensity was observed.

As the pressure was lowered, the fluorescence signal disappeared and could not be distinguished from the scattered light noise. It is probable that the argon population in
the beam is insufficient to produce the collision frequency required for the formation of large concentrations of Hg₂Ar, and thus no signal is detected.

5.3.3 Fluorescence Spectrum of the 2535.8 Å Peak of Hg₂Ar

This Hg₂Ar fluorescence spectrum was conducted with the laser fixed at 2535.8 Å, corresponding to peak 13 on Figure 5.2, and is shown in figures 5.5a and 5.5b. The atomic line is superimposed on figure 5.5a not only to show its position but also to show that the strong peak is wider than the atomic line and/or the limiting resolution of the monochromator. Table 5.4 identifies the vibronic components of the main strong peak at 2535.8 Å, and the much weaker peaks shown in more detail in Figure 5.5b.

It is possible that there are actually two overlapping spectra present here. The first spectrum is an intense peak, which may well be due to several overlapping and unresolved vibrational bands. The other spectrum is weaker and its peaks are also spaced at approximately 12.5 cm⁻¹ although the spacing is not as regular as the previous fluorescence spectra.

At very low argon pressures, the 2535.8 Å peak almost totally vanished as did all the weaker peaks. The intensities of the weaker fluorescence peaks appeared to increase more rapidly with increasing argon pressure than did the main strong peak. However, there was no discernible improvement in the intensity of the vibrational peaks for carrier gas pressures greater than 3.4 atm. Spectral runs were done for argon pressures up to 10.2 atm, the approximate pressure limit of the valve. This suggests that the emitting cluster contained at least a single rare gas atom.
Shifting the laser wavelength slightly caused the whole fluorescence spectrum to be reduced in intensity rather rapidly and eventually to completely disappear. Therefore, the upper state(s) for the fluorescence must be bound states, and the close spacing of the peaks suggests a bound-bound spectrum, although the states appear to be different from those responsible for the previous two fluorescence spectra.

The fluorescence spectrum covers a wavelength range of ≈ 12 Å with vibrational peaks spaced at approximately 1 Å, and overlaps the atomic line, the Hg$_2$

$0_u^+(6^3P_1) \leftarrow X0^+_z$, and the HgAr A0$^+ \leftarrow X0^+$ transitions, as well as the 2537.2 Å peak from the excitation spectrum. As was also the case with the 2534.3 Å peak and the 2534.6 Å peak, the fluorescence is to various higher vibrational states of the ground electronic state, which is why the fluorescence is to the red of the excitation. This results in the vibronic structure on the long wavelength side of the 2535.8 Å peak.

5.3.4 Fluorescence Spectrum of the 2536.0 Å Peak of Hg$_2$Ar

This spectrum was obtained with the laser at 2536.1 Å, offset by 0.1 Å from peak 14 of Figure 5.2. Figure 5.6 shows this spectrum. The vibronic components are listed in Table 5.5. This laser offset was chosen in order to help reduce any contribution made by the neighboring 2535.8 Å peak. The nine peaks detectable on the long wavelength side of the excitation are sharply defined and are also approximately 12.5 cm$^{-1}$ apart, suggesting that the same manifold of vibrational states is again involved in the ground electronic state.

A spectrally short (≈ 7 Å), weak continuum appears on the long wavelength side of peak 9, and is possibly due to bound-free transitions. Figures 5.3 and 5.4 have a
similar, albeit weaker continuum. It is possible that the continuum is due to unresolved bands, or that it is due to bound-free transitions to the repulsive part of the ground electronic state.

This spectrum showed the same sensitivity to carrier gas pressure as the spectrum of the neighboring peak at 2535.8 Å. At low carrier pressures, the fluorescence greatly weakened, likely due to the lack of collisions with argon atoms. At high argon pressures, the structure became more pronounced. At pressures greater than 3.4 atm, there was no appreciable increase in the intensity of the structure.

5.3.5 Fluorescence Spectrum of the 2537.2 Å Peak of Hg₃

A fluorescence spectrum was also done on the excitation spectrum’s 2537.2 Å feature, which is peak 15 of Figure 5.2, and is shown in Figure 5.7. Only a single peak resulted, located at the excitation wavelength. There does not appear to be any detectable signal on either side of the 2537.2 Å peak in excess of background noise. The single peak is asymmetric and is slightly red shaded. Since the rotational constant, \( B \), of Hg₃ will be smaller than that of Hg₂Ar due to the higher moment of inertia, the unresolved rotational structure will be narrower, which can be seen in the relatively narrow fluorescence peak. This assumes that the geometry is similar and that the argon-mercury and mercury-mercury bond lengths are comparable. The red shading could be due to unresolved rotational structure or due to two or more overlapping and unresolved vibrational bands.
The intensity of this fluorescence increased with increasing carrier gas pressure. At all carrier gas pressures, this peak is the most intense molecular feature, second in intensity only to the atomic line.

Furthermore, this peak was present and was essentially unshifted in the excitation spectra produced by Koperski et. al. [14] with both argon and krypton. This largely eliminates the possibility of it being either Hg\textsubscript{2}Ar or Hg\textsubscript{2}Kr. The most likely possibility is Hg\textsubscript{3} making a transition from an upper state to the ground state.

No upper states of either Hg\textsubscript{2}Ar or Hg\textsubscript{2}Kr are assigned in the literature. The only assigned state of Hg\textsubscript{3} is the upper state of the well known Hg\textsubscript{3} continuum at 4850 Å. It was designated by Callendar and Lai [15], and this state is probably the lower state for a series of absorption bands from 2900 Å to 4650 Å. Niefer et al. [17] reported a fluorescence band at 2170 Å, which was excited by a 4335 Å probe laser pulse which was delayed by several microseconds after a 2660 Å pump laser pulse.

Koperski et al. [14] reported the first observation of Hg\textsubscript{3} in a supersonic expansion beam, of which this is the first reported fluorescence of the 2537.2 Å peak. It seems most likely that the upper state is produced by direct absorption at 2537.2 Å from the Hg\textsubscript{3} ground vibrational state. The spectrum shown here was taken at \( x/D = 25 \) and Koperski et al. noted that collisions are generally only important for \( x/D < 20 \), so that collisions are not likely. The strength of the excitation signal and the total fluorescence is proportional to the ground state Hg\textsubscript{3} population, which will increase with greater pressures and more collisions. The Hg\textsubscript{3} ground state molecules are formed in the nozzle and the region immediately after the nozzle by collisions between Hg\textsubscript{2} molecules, Hg atoms, and Ar atoms which take away the necessary energy and momentum. Collisions
between Hg₂Ar molecules, Hg atoms, and Ar atoms may also form Hg₃ molecules. This is well justified by the dependence of the intensity of this peak on both the carrier gas pressure, and the intensity of the Hg₂ peak in figure 5.2.

No additional features were observed from 2000 Å to 8000 Å. Increasing the resolution was not possible, as reducing the slit width caused the peak to vanish. Although superficially similar to the atomic line, this peak is definitely distinct. Stepping the laser to shorter wavelengths excited the atomic line at its expected wavelength of 2536.5 Å.

5.3.6 Fluorescence Spectrum of the 2533.7 Å “Valley”

In the excitation spectrum of Figure 5.2, there appears to be at least two continuous absorption regions. The first region, which has a sharp edge at approximately 2528 Å, is due to the well known B ← X absorption continuum observed by Fuke et. al [1]. The second region between 2528 Å and 2536 Å may be a continuum, or it may arise because of overlap of the wings of the Hg₂Ar peaks and there may also be other unresolved peaks hidden in this region. Thus excitation at 2533.7 Å may correspond to exciting two or more vibrational states of the Hg₂Ar molecule. The fluorescence spectrum corresponding to this excitation is shown in figure 5.8. It has a broad continuum and an apparent sharp peak at the excitation frequency. This sharp peak is probably due to scattered laser light and is not fluorescence. A bound-free continuum spectrum from a single excited vibrational state usually has a structure on it due to “Condon Internal Diffraction” [10]. However, this structure will disappear when two or
more structured continua are emitted simultaneously from two or more excited vibrational states producing the overall envelope shown in figure 8.

There is a range of carrier gas pressures for which fluorescence is observed from both diatomic and polyatomic molecules [14]. However, increasing the argon pressure beyond 3.4 atm had little effect on the intensity of the continuum. Even with pressures of up to 10.2 atm, no additional structures were observed in the fluorescence. Further investigation of the spectral region is needed to elucidate the transitions and the species responsible for the fluorescence.

5.4 Conclusion

Hg$_2$Ar and Hg$_3$ triatomic complexes in a supersonic expansion beam have been investigated using excitation and fluorescence laser spectroscopy. The excitation range scanned was 2525 Å to 2550 Å, and the fluorescence range examined was 2000 Å to 8000 Å.

Fluorescence was observed from peaks excited at 2534.3 Å, 2534.6 Å, 2535.8 Å, 2536.0 Å, 2537.2 Å, and from the 2533.7 Å valley. Excitation peaks 9, 10, and 14 from Figure 5.2 are probably part of the same Hg$_2$Ar vibronic bands. Excitation peak 13 appears to involve different states or species to those of 9, 10, and 14. Excitation peak 15 is probably due to Hg$_3$. The “valley” appears to involve different states or species to those which are involved in the other fluorescence spectra. All observed fluorescence was confined to the UV region.

A logical extension of this research would be to examine the fluorescence spectrum of the 2537.2 Å peak and the 2533.7 Å valley using krypton as the carrier gas.
An identical fluorescence of the 2537.2 Å structure would provide further evidence that this peak is in fact due to Hg$_3$.

A different fluorescence when the 2533.7 Å “valley” is excited would allow the likely conclusion that its fluorescence is due at least in part to a different state of Hg$_2$Ar. The fluorescence is only observed at Hg and Ar pressures which give rise to the other Hg$_2$Ar spectra. However, absolute confirmation that the new species are in fact Hg$_2$Ar and Hg$_3$ must await a mass spectrum analysis.
Figure 5.1. Excitation spectra in the vicinity of the Hg atomic line. The HgAr A0⁺ ← X0⁺ and B1 ← X0⁺ transitions are clearly visible on the short and long wavelength sides respectively of the atomic line. The peaks closest to the atomic line tentatively belong to Hg₃Ar and Hg₃. P_{Ar} = 0.17 atm, P_{Hg} = 8.8 torr, D = 0.4 mm, x = 8 mm.
Figure 5.2. Excitation spectra in the vicinity of the Hg atomic line. $P_{Ar} = 3.4$ atm, $P_{Hg} = 34$ torr, $D = 0.2$ mm, $x = 5$ mm.
Figure 5.3a. Fluorescence spectrum of the 2534.3 Å peak of Hg₂Ar. \( P_Ar = 6.8 \text{ atm}, P_{Hg} = 376.2 \text{ torr}, D = 0.1 \text{ mm}, x = 7 \text{ mm}. \) The spectrometer slit width was 8 cm\(^{-1}\).

Figure 5.3b. Fluorescence spectrum of the 2534.3 Å peak of Hg₂Ar. The wavelength assignment of the peaks is listed in Table 5.2. \( P_Ar = 6.8 \text{ atm}, P_{Hg} = 376.2 \text{ torr}, D = 0.1 \text{ mm}, x = 7 \text{ mm}. \) The spectrometer slit width was 8 cm\(^{-1}\).
Figure 5.4. Fluorescence spectrum of the 2534.6 Å peak of Hg-Ar. The wavelength assignment of the peaks is listed in Table 5.3. $P_{Ar} = 6.8$ atm, $P_{Hg} = 376.2$ torr, $D = 0.1$ mm, $x = 7$ mm. The spectrometer slit width was 8 cm$^{-1}$.
Figure 5.5a. Fluorescence spectrum of the 2535.8 Å peak of Hg₂Ar. The principle peak occurs at 2535.8 Å, and the atomic line is superimposed.

Figure 5.5b. Fluorescence spectrum of the 2535.8 Å peak of Hg₂Ar. The wavelength assignment of the peaks is listed in Table 5.4. \( P_\text{Ar} = 3.4 \text{ atm, } P_\text{Hg} = 34 \text{ torr, } D = 0.2 \text{ mm, } x = 5 \text{ mm.} \) The spectrometer slit width was 8 cm⁻¹.
Figure 5.6. Fluorescence spectrum of the 2536.0 Å peak of Hg₂Ar. The wavelength assignment of the peaks is listed in Table 5.5. \( P_{Ar} = 3.4 \text{ atm, } P_{Hg} = 34 \text{ torr, } D = 0.2 \text{ mm, } \chi = 5 \text{ mm. The spectrometer slit width was } 8 \text{ cm}^{-1}. \)
Figure 5.7. Fluorescence spectrum of the 2537.2 Å peak of Hg\textsubscript{3}. P\textsubscript{Ar} = 3.4 atm, P\textsubscript{Hg} = 34 torr, D = 0.2 mm, x = 5 mm. The spectrometer slit width was 8 cm\textsuperscript{-1}.
Figure 5.8. Fluorescence spectrum after excitation at 2533.7 Å in the continuum background absorption spectrum. The single peak is located at 2533.7 Å, and the continuum has a width of approximately 73 Å. $P_{\text{Ar}} = 3.4$ atm, $P_{\text{Hg}} = 34$ torr, $D = 0.2$ mm, $x = 5$ mm. The spectrometer slit width was 8 cm$^{-1}$. 
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Table 5.1. Tentative Assignments of Vibronic Components in the Excitation Spectra. The wavelengths are given in air and the wavenumbers are given in vacuo.
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Table 5.2. Vibronic Components in the Fluorescence Spectra of the 2534.3 Å Peak of Hg$_2$Ar. The wavelengths are given in air and the wavenumbers are given in vacuo.
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<td>2543.7</td>
</tr>
<tr>
<td>12</td>
<td>39287.2</td>
<td>2544.5</td>
</tr>
<tr>
<td>13</td>
<td>39274.7</td>
<td>2545.3</td>
</tr>
</tbody>
</table>

*Table 5.3. Vibronic Components in the Fluorescence Spectra of the 2534.6 Å Peak of Hg\(_2\)Ar. The wavelenghts are given in air and the wavenumbers are given in vacuo.*
<table>
<thead>
<tr>
<th>Peak</th>
<th>( \nu ) (cm(^{-1}))</th>
<th>( \lambda ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39423.2</td>
<td>2535.8</td>
</tr>
<tr>
<td>2</td>
<td>39360.7</td>
<td>2539.8</td>
</tr>
<tr>
<td>3</td>
<td>39348.2</td>
<td>2540.6</td>
</tr>
<tr>
<td>4</td>
<td>39337.3</td>
<td>2541.3</td>
</tr>
<tr>
<td>5</td>
<td>39312.2</td>
<td>2542.9</td>
</tr>
<tr>
<td>6</td>
<td>39293.4</td>
<td>2544.1</td>
</tr>
<tr>
<td>7</td>
<td>39274.7</td>
<td>2545.3</td>
</tr>
<tr>
<td>8</td>
<td>39262.1</td>
<td>2546.1</td>
</tr>
<tr>
<td>9</td>
<td>39237.0</td>
<td>2547.7</td>
</tr>
<tr>
<td>10</td>
<td>39218.2</td>
<td>2548.9</td>
</tr>
<tr>
<td>11</td>
<td>39205.7</td>
<td>2549.7</td>
</tr>
<tr>
<td>12</td>
<td>39188.4</td>
<td>2550.8</td>
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<td>39175.9</td>
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<td>14</td>
<td>39157.0</td>
<td>2552.8</td>
</tr>
<tr>
<td>15</td>
<td>39138.2</td>
<td>2554.0</td>
</tr>
</tbody>
</table>

**Table 5.4.** Vibronic Components in the Fluorescence Spectra of the 2535.8 Å Peak of Hg\(_2\)Ar. The wavelengths are given in air and the wavenumbers are given *in vacuo*. 

71
<table>
<thead>
<tr>
<th>Peak</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\lambda$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39418.6</td>
<td>2536.1</td>
</tr>
<tr>
<td>2</td>
<td>39398.2</td>
<td>2537.4</td>
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<tr>
<td>3</td>
<td>39385.8</td>
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<td>4</td>
<td>39373.2</td>
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<td>2539.8</td>
</tr>
<tr>
<td>6</td>
<td>39348.2</td>
<td>2540.6</td>
</tr>
<tr>
<td>7</td>
<td>39337.3</td>
<td>2541.3</td>
</tr>
<tr>
<td>8</td>
<td>39324.8</td>
<td>2542.1</td>
</tr>
<tr>
<td>9</td>
<td>39312.2</td>
<td>2542.9</td>
</tr>
</tbody>
</table>

Table 5.5. Vibronic Components in the Fluorescence Spectra of the 2536.0 Å Peak of Hg$_2$Ar. The laser was slightly offset to 2536.1 Å to reduce contributions from the nearby 2535.8 Å peak. The wavelengths are given in air and the wavenumbers are given in vacuo.
Appendix 1: Frequency Doubling

When an electric field is applied to a material, a dipole moment per unit volume \( P = \chi \varepsilon_0 E \) (A1.1) is induced, where \( \chi \) is the electric susceptibility given by \( (\varepsilon/\varepsilon_0) - 1 \). If the material is symmetric, then \( \chi \) is a scalar. However, if the material is non-symmetric (anisotropic), then \( \chi \) is a tensor with elements \( (\chi_1, \chi_2, \chi_3, \ldots) \). This is needed to represent different polarizations of the material, as the electric field is applied at different angles to the crystal axis. For intense electric fields, (A1.1) must be modified to account for non-linear interactions. Thus:

\[
P = \varepsilon_0 \sum_n \chi_n E^n \quad \text{(A1.2)}
\]

Equation (A1.2) assumes an idealization in which the medium is without dispersion or losses.

If an anisotropic material \( (\chi_2 \neq 0) \) is exposed to an intense laser beam with fundamental frequency \( \omega_1 \), the emergent beam will contain both the fundamental frequency and the second harmonic \( (\omega_2 = 2\omega_1) \).

The incident oscillating electric field can be described by (A1.3).

\[
E = E_o \exp(i\omega t) + E_o^* \exp(-i\omega t) \quad \text{(A1.3)}
\]

The polarization for the second harmonic can be written as (A1.4):

\[
P_2 = 2\varepsilon_0 \chi_2 \left( E^* E + E^2 \exp(-2i\omega t) + E^{*2} \exp(2i\omega t) \right) \quad \text{(A1.4)}
\]
The terms $E^2 \exp(-2i\omega t)$ and $E^2 \exp(2i\omega t)$ contain the term $2\omega$ (the second harmonic).

The $E^*E$ term (optical rectification), is a DC electric field without oscillating electromagnetic radiation, and thus does not contribute to frequency doubling. In order to produce a "useable" second harmonic, the laser must be intense, because $\chi_2 < \chi_1$.

After the second harmonic is created, it must be separated from the fundamental. To accomplish this, both beams are sent through a prism, and because they have different wavelengths, they are refracted at different angles. The second harmonic is then passed through a second prism, where it is directed to UV mirrors and into the chamber. The second prism is used prevent optical misalignment as the dye laser grating is rotated. The distance between the prisms is approximately 21 cm, resulting in little to no travel of the laser spot in the chamber. If the second prism was not used, significant laser spot travel would occur, as the "optical lever arm" would be several meters.
Appendix 2: Velocity Distribution and Mean Free Path

The velocity distribution in a supersonic beam is the superimposition of a Maxwellian function and the mean velocity. Therefore:

\[ f(v) = \left( \frac{v}{\alpha} \right)^3 \exp \left[ -\left( \frac{v-u}{v} \right)^2 \right] \]  \hspace{1cm} (A2.1)

Where \( f(v) \) is the velocity distribution function

\( v \) is the particle velocity

\( u \) is the mean particle velocity

\( \alpha = (2kT/m)^{1/2} \)

As expected, \( f(v) \) decreases with increasing temperature, and hence local Mach number. Also, the distribution is wider with heavier particles than with light ones.

The mean free path within the beam is highly non-trivial to calculate. However, the region contained by the barrel shocks and Mach disk shock is essentially collision-free\(^1\) (see Figure A2.1). Using equation 1.4, the location of the Mach disk is easily determined. For a nozzle pressure of 3.4 atm (50 psi), and a background pressure of \( 10^3 \) torr, \( x_m/D \approx 1077 \). For a 200 \( \mu \)m nozzle, the Mach disk is located \( \approx 215 \) mm from the aperture. Laser excitation occurred 5 mm from the aperture, well within the zone of silence.

---

\(^1\) This region has been termed the *zone of silence*, in which the isentropic expansion is independent of the background pressure. Flow within this zone is "unaware" of external conditions.
Before laser excitation occurs, steady state conditions must exist in the beam. The minimum opening times for a pulsed valve in order to achieve a steady state are dependent upon the type of carrier gas, the carrier gas pressure, the temperature, and the nozzle diameter. The minimum opening times for a valve through which (i) 200 torr and (ii) 2000 torr of Argon pass (0.5 mm nozzle) at 300 K are 1.9 $\mu$s and 3.1 $\mu$s respectively [37].

The mean free path within the evacuated chamber is easily obtained from

$$l = \left( \frac{\sqrt{2}N\pi r^2}{N} \right)^{\frac{1}{3}} \quad (A2.2)$$

where $l$ is the mean free path, $N$ is the number density of air molecules in the chamber (number of air molecules/cm$^3$), and $r$ is the diameter of the air molecules.

At the conditions of $10^3$ torr and 420 K, the vapor density of air is $8.9 \times 10^{13}$ cm$^{-3}$. Taking the radius of air molecules to be $1.7 \times 10^{-4}$ cm, the resultant mean free path is 8.7 cm, far in excess of the maximum laser excitation distance of 2.5 cm. Thus, $10^3$ torr is an ample vacuum, and diffusion pumping is not necessary.
Figure A2.1. Supersonic gas expansion. The flow is subsonic in the gas source, and supersonic in the zone of silence.
Appendix 3: CCD Control Program

REM This program operates an HR 320 monochromator, a tuneable dye laser and its doubling crystal
REM This program is written in Spectrum Basic®.

REM Declare variables
INT MONOTYPE
INT SPECTRALINTEGER320
INT LOOPCOUNTER
FLOAT MONOCURRENTWAVE320
FLOAT MONOSTARTWAVE320
FLOAT MONOENDWAVE320
FLOAT MONOCOUNTDIFF320
FLOAT SPECTRALCOVERAGE320
FLOAT SPECTRALRANGE320
FLOAT INCREMENTS320
FLOAT SPECTRALFLOTA320
FLOAT LASERCURRENTCOUNT
FLOAT LASERSTARTCOUNT
FLOAT LASERENDCOUNT
FLOAT LASERSTEP320
FLOAT LASERDIFF
FLOAT LASERRANGE
FLOAT LASERINCREMENTS
FLOAT DOUBLERSTEP
FLOAT OLDCOUNTER
FLOAT NEWCOUNTER
FLOAT X
FLOAT AMOUNTMONODOWN320

REM Clear Screen
LET tmp = REDIRPRT( 500 )
FOR J = 1 TO 100
PRINT "",J,0,0,5
NEXT J
PRINT "PRINCETON INSTRUMENTS DYE LASER/SPECTROMETER CONTROLLER by Jeff S. Lee",6,7,0,5
PRINT "Enter current monochromator wavelength (Angstroms)",25,10,0,5
INP MONOCURRENTWAVE320
PRINT "Enter monochromator starting wavelength (Angstroms)",30,10,0,5
INP MONOSTARTWAVE320
PRINT "Enter monochromator ending wavelength (Angstroms)",35,10,0,5
INP MONOENWWAVE320

REM Calculate how many times the monochromator will have to be advanced for each laser wavelength
LET SPECTRALCOVERAGE320 = 200
LET SPECTRALRANGE320 = MONOENWWAVE320 - MONOENWWAVE320
LET SPECTRALINTEGER320 = SPECTRALRANGE320/SPECTRALCOVERAGE320
LET INCREMENTS320 = SPECTRALINTEGER320 + 1

REM Clear screen and input data for laser
FOR JJ = 10 TO 100
PRINT ",JJ,0,0,5
NEXT JJ

PRINT "Enter current laser counter value",20,10,0,5
INP LASERCURRENTCOUNT
PRINT "Enter laser starting counter value",25,10,0,5
INP LASERSTARTCOUNT
PRINT "Enter laser ending counter value",30,10,0,5
INP LASERENDCOUNT
PRINT "Enter laser step size",35,10,0,5
INP LASERSTEPSIZE

REM Move laser motor to start position
LET tmp = REDIRPR( PRINTERPORT )
PRINT CHR(0)
LET LASERDIFF = LASERSTARTCOUNT - LASERCURRENTCOUNT
IF LASERCURRENTCOUNT < LASERSTARTCOUNT THEN
FOR JJ = 1 to LASERDIFF*10
PRINT CHR(2)
PRINT CHR(10)
PRINT CHR(2)
NEXT JJ
PRINT CHR(0)
ELSEIF LASERCURRENTCOUNT > LASERSTARTCOUNT THEN
FOR KK = 1 to ABS(LASERDIFF)*10
PRINT CHR(1)
PRINT CHR(9)
PRINT CHR(1)
NEXT KK
PRINT CHR(0)
ENDIF

REM Calculate how far to move doubler to correspond to laser's start position
LET X = ABS(LASERDIFF)
LET DOUBLERSTEP = -.0001228*X*X + 1.27929*X

REM  Now move doubler to correct to laser start position
IF LASERDIFF > 0 THEN
FOR QQ = 1 TO DOUBLERSTEP*10
PRINT CHR(16)
PRINT CHR(48)
PRINT CHR(16)
NEXT QQ
PRINT CHR(0)
ELSEIF LASERDIFF < 0 THEN
FOR QQQ = 1 TO ABS(DOUBLERSTEP)*10
PRINT CHR(1)
PRINT CHR(33)
PRINT CHR(1)
NEXT QQQ
PRINT CHR(0)
ENDIF

REM  Move monochromator motor to start position
rem LET tmp = REDIRPRT( PRINTERPORT )
LET MONOCOUNTDIFF320 = MONOSTARTWAVE320 - MONOCURRENTWAVE320
IF MONOCURRENTWAVE320 < MONOSTARTWAVE320 THEN
FOR J= 1 to MONOCOUNTDIFF320*10
PRINT CHR(1)
PRINT CHR(5)
PRINT CHR(1)
NEXT J
PRINT CHR(0)
ELSEIF MONOCURRENTWAVE320 > MONOSTARTWAVE320 THEN
FOR K = 1 to ABS(MONOCOUNTDIFF320)*10
PRINT CHR(2)
PRINT CHR(6)
PRINT CHR(2)
NEXT K
PRINT CHR(0)
ENDIF

REM  Set up loop that advances laser and doubler together

LET DOUBLERSTEP = 0
LET NEWCOUNTER = 0
LET OLD COUNTER = 0
LET LASERENDCOUNT = LASERENDCOUNT - LASERSTARTCOUNT
LET LASERSTARTCOUNT = 0
LET LASERRANGE = LASERENDCOUNT
LET LASERINCREMENTS = LASERRANGE/LASERSTEPSIZE*10

LET LOOPCOUNTER = 1

REM Initiate loop that moves laser across excitation range
IF LASERRANGE > LASERSTEPSIZE/10 THEN
FOR LL = 1 TO LASERINCREMENTS + 1

REM Move HR 320 across spectral intervals to be measured
IF SPECTRALRANGE320 > SPECTRALCOVERAGE320 THEN
FOR L = 1 TO INCREMENTS320

REM RUN DATA COLLECTION ROUTINE HERE

REM Advance loop counter for file name
let LOOPCOUNTER = LOOPCOUNTER + 1

REM Advance monochromator to next interval to take readings
rem let tmp = REDIRPRT(PRINTERPORT)
FOR M = 1 TO SPECTRALCOVERAGE320*10
PRINT CHR(1)
PRINT CHR(5)
PRINT CHR(1)
NEXT M
PRINT CHR(0)
NEXT L
PRINT CHR(0)

REM RUN DATA COLLECTION ROUTINE HERE

REM Advance loop counter for file name
let LOOPCOUNTER = LOOPCOUNTER + 1
IF LL > LASERINCREMENTS THEN
PRINT CHR(0)
STOP
ENDIF
ELSE

REM In this event, desired spectral range is less than spectral coverage.
REM Therefore, collect data here and advance laser to new position

REM RUN DATA COLLECTION ROUTINE HERE

let LOOPCOUNTER = LOOPCOUNTER + 1
IF LOOPCOUNTER > LASERINCREMENTS + 1 THEN
PRINT CHR(0)
STOP
ENDIF
ENDIF

FOR MMMM = 1 TO LASERSTEPSIZE
PRINT CHR(2)
PRINT CHR(10)
PRINT CHR(2)
NEXT MMMM
PRINT CHR(0)
LET NEWCOUNTER = OLD COUNTER + LASERSTEPSIZE/10

REM Calculate amount to move doubler
LET X = NEWCOUNTER
LET DOUBLERSTEP = -.0001228*X*X + 1.27929*X

REM Now move doubler to correct for new laser position
FOR QQ = 1 TO DOUBLERSTEP*10
PRINT CHR(16)
PRINT CHR(48)
PRINT CHR(16)
NEXT QQ
PRINT CHR(0)

IF SPECTRALRANGE320 > SPECTRALCOVERAGE320 THEN
REM Reset the monochromator to its bottom limit for next laser position
WAIT 1000
LET tmp = REDIRPRT( PRINTERPORT )
LET AMOUNTMONODOWN320 = INCREMENTS320*SPECTRALCOVERAGE320
FOR ICQ = 1 TO AMOUNTMONODOWN320*10
PRINT CHR(2)
PRINT CHR(6)
PRINT CHR(2)
NEXT ICQ
PRINT CHR(0)
ENDIF

REM Advance loop for laser position
NEXT LL

REM Collect data here for final laser position
REM RUN DATA COLLECTION ROUTINE HERE

let LOOPCOUNTER = LOOPCOUNTER + 1
PRINT CHR(0)
ELSE

REM In this event, the laser does not move

IF SPECTRALRANGE320 > SPECTRALCOVERAGE320 THEN
FOR L = 1 TO INCREMENTS320

REM Advance loopcounter for naming of file

REM RUN DATA COLLECTION ROUTINE HERE

REM Advance loop counter for file name
let LOOPCOUNTER = LOOPCOUNTER + 1

REM Advance monochromator to next interval to take readings
rem let tmp = REDIRPRT( PRINTERPORT )
FOR M = 1 TO SPECTRALCOVERAGE320*10
PRINT CHR(1)
PRINT CHR(5)
PRINT CHR(1)
NEXT M
PRINT CHR(0)
NEXT L
PRINT CHR(0)

REM Take last set of readings here
REM RUN DATA COLLECTION ROUTINE HERE

REM Advance loop counter for file name
let LOOPCOUNTER = LOOPCOUNTER + 1
IF LOOPCOUNTER > LASERINCREMENTS THEN
PRINT CHR(0)
STOP
ENDIF
ELSE

REM In this event, desired spectral range is less than spectral coverage.
REM Therefore, collect data here and advance laser to new position
REM RUN DATA COLLECTION ROUTINE HERE

let LOOPCOUNTER = LOOPCOUNTER + 1
IF LOOPCOUNTER > LASERINCREMENTS + 1 THEN
PRINT CHR(0)
STOP
ENDIF
ENDIF

FOR MMMM = 1 TO LASERSTEPsize
  PRINT CHR(2)
  PRINT CHR(10)
  PRINT CHR(2)
  NEXT MMMM
  PRINT CHR(0)
  LET NEWCOUNTER = OLDCOUNTER + LASERSTEPsize/10

  REM Calculate amount to move doubler
  LET X = NEWCOUNTER
  LET DOUBLERSTEP = -.0001228*X*X + 1.27929*X

  REM Now move doubler to correct for new laser position
  FOR QQ = 1 TO DOUBLERSTEP*10
    PRINT CHR(16)
    PRINT CHR(48)
    PRINT CHR(16)
    NEXT QQ
    PRINT CHR(0)

IF SPECTRALRANGE320 > SPECTRALCOVERAGE320 THEN
  REM Reset the monochromator to its bottom limit for next laser position
  WAIT 1000
  LET tmp = REDIRPRT(PRINTERPORT)
  LET AMOUNTMONODOWN320 = INCREMENTS320*SPECTRALCOVERAGE320
  FOR ICQ = 1 TO AMOUNTMONODOWN320*10
    PRINT CHR(2)
    PRINT CHR(6)
    PRINT CHR(2)
    NEXT ICQ
    PRINT CHR(0)
ENDIF
ENDIF
Data Collection Routine

let outfilenum = 1
int newname
let tmp = ADDVAREXP( LOOPCODENTER, newname )
let frames = 1
open newname for output as outfilenum
let tmp = INIT1FRAME

int xprog
int yprog
int fastread
int proglines
int progsfrips
int stripsinfile
let stripsinfile = 0

let r undone = GETPROGXY( xprog, yprog, fastread, proglines, progsfrips )
unint s( yprog, xprog )

let tmp = START130
let framecntr = 0
let a = WAIT1FRAME
let tmp = STOP130
let a = GETFULLFRAME( s )
  rem print a,80,10,0,11
  rem print " COLLECTING DATA ",0+LOOPCOUNTER,0,0,11+LOOPCOUNTER
let tmp = WRITEFRAME( outfilenum,s )
  rem print "it has written",10+LOOPCOUNTER,10,0,11+LOOPCOUNTER

let a = SETHEADER( outfilenum, 3, 3 )
let a = SETHEADER( outfilenum, 4, xprog )
float totalstrips
let totalstrips = ( 1.0 * yprog ) * ( 1.0 * frames ) + stripsinfile
let a = SETHEADER( outfilenum, 5, totalstrips )
let a = SETHEADER( outfilenum, 6, yprog )
let a = SETHEADER( outfilenum, 7, 1 )
close outfilenum
let tmp = RESET1FRAME
ERASE s
ERASE totalstrips
Appendix 4: Laser Control Program

REM
REM
REM
REM This program controls a tuneable dye laser and its doubling crystal
REM By Jeff S. Lee
REM University of Windsor
REM January 1999
REM
REM
REM
REM This program is written in Microsoft Basic©
REM
REM Clear screen to begin
CLS

REM Input laser counter information
PRINT "Enter current laser counter value"
INPUT LASC

FOR qq = 1 TO 3
PRINT
NEXT qq

PRINT "Enter laser starting counter value"
INPUT LASS

FOR qq = 1 TO 3
PRINT
NEXT qq

PRINT "Enter laser ending counter value"
INPUT LASE

FOR qq = 1 TO 3
PRINT
NEXT qq

PRINT "Enter laser step size"
INPUT LASST
LET DBPULSE = 0
REM  Move laser motor to start position
LET LASDIFF = LASS - LASC
IF LASC < LASS THEN
GOSUB setup2
FOR JJJ = 1 TO LASDIFF * 10
GOSUB clock2
NEXT JJJ
END IF
IF LASC > LASS THEN
GOSUB setdwn2
FOR KK = 1 TO ABS(LASDIFF) * 10
GOSUB clock2
NEXT KK
END IF

REM STOP

REM  Calculate how far to move doubler to correspond to laser's start position
LET X = ABS(LASDIFF)
LET DOUBSTEP = -.0001228 * X * X + 1.27929 * X

REM  Now move doubler to correct for laser start position
IF LASDIFF > 0 THEN
GOSUB setup3
FOR qq = 1 TO DOUBSTEP * 10
GOSUB clock3
NEXT qq
END IF
IF LASDIFF < 0 THEN
GOSUB setdwn3
FOR QQQC = 1 TO ABS(DOUBSTEP) * 10
GOSUB clock3
NEXT QQQC
END IF

REM STOP

REM  Wait to see spectrum produced

PRINT "Press Esc to move laser to next position";
DO
LOOP UNTIL INKEYS$ = CHR$(27)
REM Set up loop that advances laser and doubler together

LET OLDCOUN = 0
LET DOUBSTEP = 0
LET NEWCOUN = 0
LET PULSES = 0
LET PULSEY = 0

LET LASRANGE = LASE - LASS
LET lasinc = LASRANGE / LASST * 10

REM Move laser across excitation range
FOR LL = 1 TO lasinc + 1
IF LL > lasinc THEN STOP
GOSUB setup2
FOR MMMM = 1 TO LASST
GOSUB clock2
PULSEY = PULSEY + 1
NEXT MMMM

REM Calculate amount that doubler will move
LET X = LASST / 10
LET DOUBSTEP = -.0001228 * X * X + 1.27929 * X

REM Now move doubler to correct for new laser position
GOSUB setup3
FOR qqr = 1 TO DOUBSTEP * 10
GOSUB clock3
LET PULSES = PULSES + 1
NEXT qqr

LET POSSHDBE = -.0001228 * (PULSEY / 10) ^ 2 + 1.27929 * (PULSEY / 10)
PRINT LL, PULSES / 10, INT(PULSES / 10), POSSHDBE, INT(POSSHDBE)
IF PULSES < POSSHDBE * 10 THEN
FOR JEFF = 1 TO POSSHDBE * 10 - PULSES
GOSUB setup3
GOSUB clock3
LET PULSES = PULSES + 1
NEXT JEFF
END IF

REM Wait to see spectrum produced
PRINT "Press Esc to move laser to next position"
DO
LOOP UNTIL INKEY$ = CHR$(27)
REM Advance loop for laser position
NEXT LL

setup2: GOSUB rd
    OUT &H378, (p% OR &H2)
    RETURN

setdwn2: GOSUB rd
    OUT &H378, (p% AND &HFD)
    RETURN

clock2: GOSUB rd
    OUT &H378, (p% OR &H8)
    OUT &H378, (p% AND &HF7)
    RETURN

setup3: GOSUB rd
    OUT &H378, (p% OR &H10)
    RETURN

setdwn3: GOSUB rd
    OUT &H378, (p% AND &HEF)
    RETURN

clock3: GOSUB rd
    OUT &H378, (p% OR &H20)
    OUT &H378, (p% AND &HDF)
    RETURN

rd:     p% = INP(&H378)
        RETURN
References


33. Ibid. p.354
Vita Auctoris

I was born on November 13, 1964 in Toronto, Canada. Graduating from W.L. Mackenzie C.I. in 1983, I was self-employed until 1986 when I enrolled in York University. I graduated in 1991 with an H.B.Sc in physics, and was awarded the Denise Hobbins prize for the highest mark in first year physics by a physics major. In 1993, I graduated on the Dean’s Honour List from the Faculty of Education at the University of Western Ontario.

For the two years that followed, I taught International Baccalaureate physics at the Inter*American Academy in Guayaquil, Ecuador. In 1994, I received an education scholarship from the University of Houston to attend their Aerospace Education Workshop for International Teachers held at the Johnson Space Center. The following year, I moved back to Toronto and taught high school mathematics at the Community Hebrew Academy of Toronto for one year.

Then, I returned to further my education with a M.Sc in physics from the University of Windsor. Upon its completion, I intend to continue my teaching career at both Canadian and International Schools.