Spectroscopic studies of the internal modes of amino-aromatics by fluorescence excitation and dispersed emission in supersonic jet
by Shuxin Yan

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University
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Abstract:
A systematic study for the NH2 inversional mode in aniline and para substituted anilines has been performed using the techniques of the fluorescence excitation and dispersed emission in supersonic jet. The transitions of the nitrogen inversion mode in aniline and para substituted anilines have been assigned in both the fluorescence excitation and dispersed emission spectra, which are strongly supported by the evidence of a large deuterium shift, the presence of a strong hot band, and the intense second overtone transition of the amino inversion in the excitation spectra of all the aniline molecules. The potential surface of each aniline has been fit using the observed inversional levels in both the ground and excited states. The molecular structure of each aniline has been investigated based on the experimental results.

The NH2 torsional transition is assigned in the excitation spectrum of each aniline molecule for the first time. The absence of a torsional hot band and no observable tunneling splitting in the NH2 torsional mode indicates that the NH2 torsion mode in the anilines must have a very high first quanta in the ground state.

The mechanism of I20 and T20 splittings in the excitation spectrum of p-toluidine has been explained by using molecular symmetry. The splittings are caused by the torsion - torsion coupling between the NH2 and CH3 groups.

The structure of p-amino-p'-methyl-trans-stilbene (PPTS) has been studied by spectroscopic methods and X-ray diffraction. The nearly planar geometry of the proton donor in the PPTS crystal dimer provides important evidence that the structure of gas phase PPTS is planar in the ground state. The absence of the hot band and I20 in the excitation spectrum of PPTS indicates that the potential surface of PPTS must be a single well in both states, which is consistent with the X-ray result. The methyl torsional transition frequencies are significantly reduced by the para substitution of the NH2 group in PPTS (as compared to p-methyl-trans-stilbene) which is attributed to the electron donating nature of the NH2 group and the lone pair in the amino group involved in the $\pi$-cloud of PPTS changing the methyl hyperconjugation with the $\pi$system.

# SPECTROSCOPIC STUDIES OF THE INTERNAL MODES OF AMINO-AROMATICS BY FLUORESCENCE EXCITATION AND DISPERSED EMISSION IN SUPERSONIC JET

by

Shuxin Yan

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# ABSTRACT

A systematic study for the $NH_2$ inversional mode in aniline and para substituted anilines has been performed using the techniques of the fluorescence excitation and dispersed emission in supersonic jet. The transitions of the nitrogen inversion mode in aniline and para substituted anilines have been assigned in both the fluorescence excitation and dispersed emission spectra, which are strongly supported by the evidence of a large deuterium shift, the presence of a strong hot band, and the intense second overtone transition of the amino inversion in the excitation spectra of all the aniline molecules. The potential surface of each aniline has been fit using the observed inversional levels in both the ground and excited states. The molecular structure of each aniline has been investigated based on the experimental results.

The $NH_2$ torsional transition is assigned in the excitation spectrum of each aniline molecule for the first time. The absence of a torsional hot band and no observable tunneling splitting in the $NH_2$ torsional mode indicates that the $NH_2$ torsion mode in the anilines must have a very high first quanta in the ground state.

The mechanism of $I^2_0$ and $T^2_0$ splittings in the excitation spectrum of p-toluidine has been explained by using molecular symmetry. The splittings are caused by the torsion - torsion coupling between the $NH_2$ and $CH_3$ groups.

The structure of p-amino-p'-methyl-trans-stilbene (PPTS) has been studied by spectroscopic methods and X-ray diffraction. The nearly planar geometry of the proton donor in the PPTS crystal dimer provides important evidence that the structure of gas phase PPTS is planar in the ground state. The absence of the hot band and $I^2_0$ in the excitation spectrum of PPTS indicates that the potential surface of PPTS must be a single well in both states, which is consistent with the X-ray result. The methyl torsional transition frequencies are significantly reduced by the para substitution of the $NH_2$ group in PPTS (as compared to p-methyl-trans-stilbene) which is attributed to the electron donating nature of the $NH_2$ group and the lone pair in the amino group involved in the $\pi$-cloud of PPTS changing the methyl hyperconjugation with the $\pi$ system.

# INTRODUCTION

Internal modes in molecules have intrinsic interest for chemists due to several special features compared to skeletal modes. First of all, internal modes do not conform to the harmonic approximation. The anharmonicities can make the spectral analysis more difficult. Also most internal modes are nonrigid vibrations for which the point group will not work properly. The correct symmetry description for nonrigid molecules is molecular symmetry groups which is constructed from nuclear permutations which reflect the motions of the nonrigid modes[1-3] Additionally, the potential surfaces of many internal modes have multiple minima and tunneling often occurs between the wells which causes vibrational level splitting. Lastly, internal modes usually are large amplitude motions which are easily perturbed by other substituents. In the multiply substituted aromatics, the interaction between the groups can be easily achieved through the conjugated $\pi$ system even with significant separation.

Aniline and para substituted anilines, such as p-methyl-aniline and p-fluoroaniline, have been studied for many years,[4-24] Brand et al assigned the transitions of aniline and deuterated aniline in the room temperature gas phase spectrum, however, the large rotational broadening and congestion from

hot bands prevented them from discerning close lying transitions, such as the three peaks around 550 cm$^{-1}$ in the deuterated aniline spectrum. The significant difference of the fluorescence excitation spectrum of p-toluidine in a supersonic expansion and at room temperature can be seen in Figure 1. The very broad band widths and a large number of congestions cannot give rise to the correct transitional frequencies in the room temperature spectrum. Meanwhile, the weak transitions cannot be seen in the spectrum. However, the spectrum taken in a supersonic jet has no congestions and provides very accurate transition frequencies. The weak transitions appear obviously in the jet-cooled spectrum. Other workers have used a supersonic expansion to cool the molecules thereby reducing line widths and congestion due to hot bands but they didn't use other powerful techniques to support their assignments. This thesis presents a symmetric study of aniline, and some substituted aniline using the techniques of expansion cooling under different conditions to reveal hot bands, fluorescence excitation, dispersed emission, and isotopic substitution.

## Nitrogen Inversion and NH$_2$ Torsion

The structure of aniline in the ground state has the equilibrium position of the two NH$_2$ protons out of the ring plane and the angle between the ring plane and the plane formed by NH$_2$ was estimated to be around 42°.[6,12] The motion of the two protons up and down about the ring plane is called the

p-toluidine

cm-1
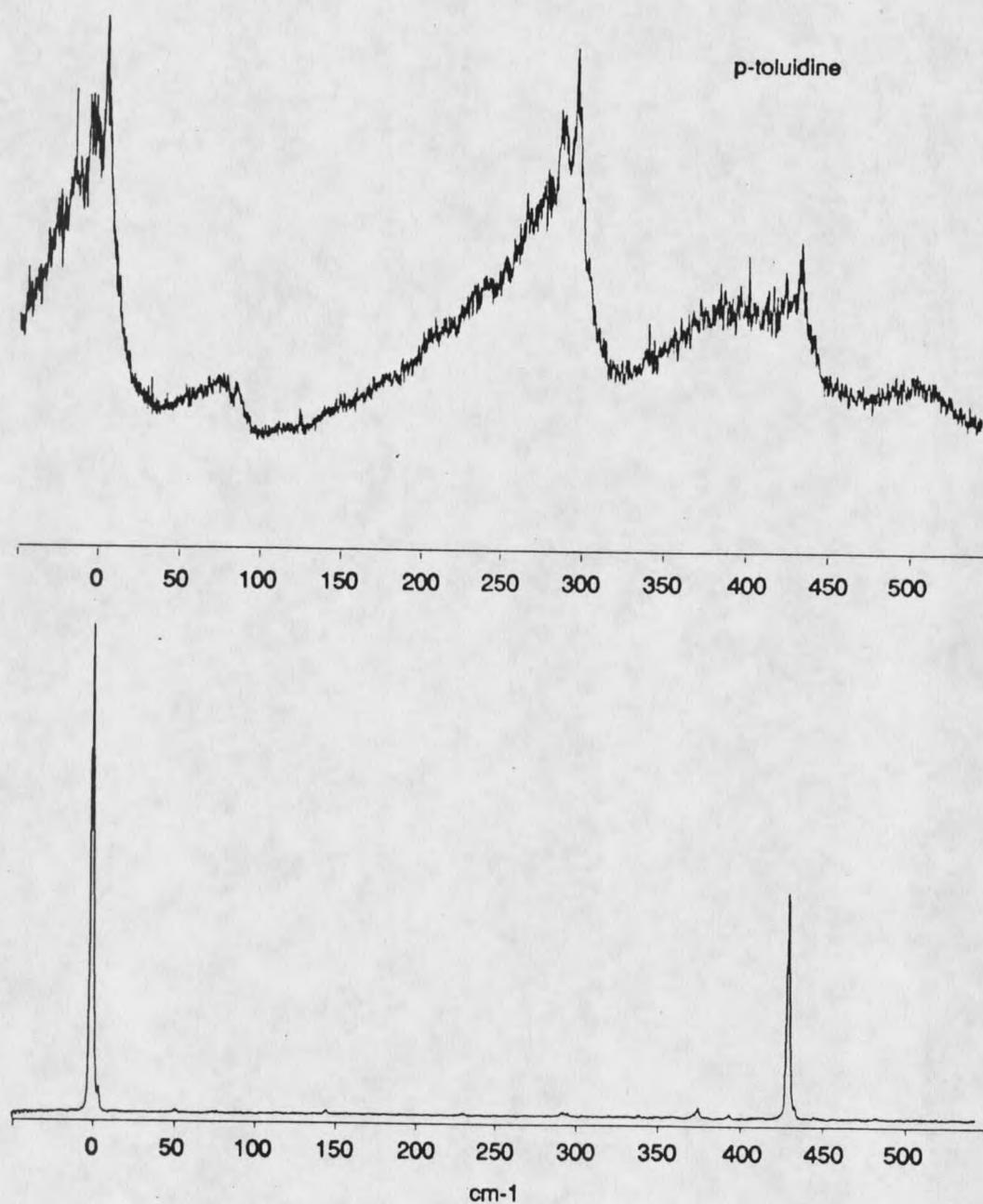
Figure 1. Comparison of the excitation spectrum of aniline (top trace) at room temperature with the one (bottom trace) in a supersonic jet (7 bar backing pressure).

nitrogen inversion mode which is analogous to the "umbrella" motion in ammonia. The nitrogen inversion is a large amplitude motion and has a double minimum potential in aniline.

Kydd and Krueger[6] fit the barrier height to nitrogen inversion as 526 $cm^{-1}$ based on far-infrared results. The first inversion quanta of aniline and deuterated aniline in the ground state were measured at 40.8 $cm^{-1}$ and 13.4 $cm^{-1}$ respectively.[6] The large deuterium shift is very convincing evidence for their assignment. The second quanta of nitrogen inversion in aniline and deuterated aniline were assigned as 423.8 and 337.5 $cm^{-1}$ respectively.[6]

The barrier height and the inversion levels of aniline in the excited state were studied by several groups.[4,8,13-15] Although there were some differences in calculated barriers (Brand et al[4] fit the barrier with 24 $cm^{-1}$ and Hollas et al[8] fit it to be zero), the results indicate that the barrier for inversion in the excited state should be extremely low. Our result for the inversional barrier height in the excited state is in good agreement with the fit by Hollas et al. Thus, the structure of the amino group in the excited state is expected to be planar. Hollas and co-workers rejected Ito's assignment[13] for the transitions around 352 $cm^{-1}$ as $I_0^1$ in the excitation spectrum of aniline because this transition is restricted by the even quanta selection rules of nitrogen inversion. In the deuterated aniline, the deuterium shift for the inversion transitions are significant. The $I_1^1$ and $I_0^2$ were measured at 239.3 and 546.8 $cm^{-1}$ respectively.[8] The peaks around 352 $cm^{-1}$ in the excitation spectrum of deuterated aniline do

not have significant shifts. This indicates that the peaks around 352 cm$^{-1}$ do not contribute to the NH$_2$ group. Later, Bacon and Hollas[16] proved the doublet splitting for the transitions around 352 cm$^{-1}$ to be a Darling-Dennison resonance and assigned them as $10b_0^2$ and $16a_0^2$ for the low and high wavenumber components, respectively. The first and second quanta of nitrogen inversion in the excited state were measured at 333.4 and 760.2 cm$^{-1}$ for aniline and 246.7 and 545.4 cm$^{-1}$ for deuterated aniline.[8]

The nitrogen inversion has also been studied in some para substituted anilines, such as p-fluoroaniline,[12] p-toluidine,[17-19] and p-trifluoromethyl-aniline.[20] The inversion levels and potential in p-fluoroaniline and p-toluidine are very similar to those in aniline. This is expected because the inversion mode is relatively independent of the other modes in the molecule. However, the first quanta and barrier height of nitrogen inversion in p-trifluoromethyl-aniline were measured to be 72.0 cm$^{-1}$ and 373 cm$^{-1}$ in the ground state, respectively.[20] Compared with 40.8 cm$^{-1}$ of the first quanta and 525 cm$^{-1}$ of the barrier in aniline, this change is rather large. This may perhaps be due to the highly electron withdrawing nature of the CF$_3$ group. The resonance enhanced two photon ionization spectra of p-fluoroaniline and p-toluidine were reported by Lubman and co-workers,[21] but they did not assign the inversion transitions. The peak at 775 cm$^{-1}$ in the p-fluoroaniline spectrum and the peak at 707 cm$^{-1}$ in the p-toluidine spectrum were assigned as $12_0^1$. We disagree with this assignment because both of these transitions can be attributed to internal

modes of $NH_2$ group. The peak at 775 cm$^{-1}$ in the p-fluoroaniline spectrum is very similar to the $I_0^2$ transition in aniline and should be assigned that way. Further evidence for this assignment will be provided later in this thesis. However, we also observe a different frequency for this transition, 759.6 cm$^{-1}$ instead of 775 cm$^{-1}$. We question the assignment for the 707 cm$^{-1}$ peak in Ref. 21 on the basis of our deuterated p-toluidine work presented in detail later. This peak is shifted in our deuterated p-toluidine spectrum by more than 140 cm$^{-1}$ so it cannot be a transition from a skeleton mode and must be due to an internal motion of the $NH_2$ group. Smalley and co-workers[19] assigned the peak at 734 cm$^{-1}$ in the excitation spectrum of p-toluidine as $I_0^2$. This peak, however, is only one member of a quartet that appears around this frequency. The observed inversion levels are listed in Table 1.

Table 1. The Inversion Levels of Nitrogen Inversion in Aniline and Para-Substituted Anilines.(cm$^{-1}$)

| State | Assignment | aniline | aniline-ND$_2$ | p-Fluoroaniline | p-Toluidine |
|---|---|---|---|---|---|
| Ground | | | | | |
| $I_1$ | 40.8[6] | 13.4[6] | 31.7[12] | 33.2[17] | |
| $I_2$ | 423.8 | 337.5 | 437.9 | 434.1 | |
| $I_3$ | 700.1 | 457.0 | 708.4 | 684.2 | |
| | Barrier | 525.9 | 543.4 | 596.4 | 588 |
| Excited | | | | | |
| $I^1$ | 333.4[8] | 252.7[8] | --- | --- | |
| $I^2$ | 760.2 | 546.8 | --- | 737.3[19] | |
| | $I^3$ | 1224.6 | 873.8 | --- | --- |
| Barrier | 0 | 0 | --- | --- | |

It is clear that the inversional levels have very different spacings. Thus, the

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nitrogen inversion mode is very anharmonic in both states.

NH$_2$ torsion, where the two hydrogens bonded to nitrogen twist around N-C bond, is another internal motion of the amino group in the anilines. The NH$_2$ torsional transition in the ground state was claimed by Fateley and coworkers[22] to be at 285 cm$^{-1}$ but was assigned as 277.3 cm$^{-1}$ by Nicolaison et al.[12] The NH$_2$ torsional barrier was estimated to be 2005 cm$^{-1}$ which seems to be acceptable.[12] To our knowledge, no NH$_2$ torsional transitions have been assigned in the excited state. The potential function for NH$_2$ torsion around the C-N bond is assumed to be of the cos2$\alpha$ type and one quanta transitions of the amino torsional mode are forbidden, both in the IR and as vibronic transition. The transition level was observed in the far IR[12] in combination with (T$_1$ + I$_1$) and a difference band (T$_1$ - I$_1$) In the excitation spectra of aniline and p-toluidine, however, no cross combination transitions T$_i$I$_j$ (i+j = even number) have ever been found. This is because evaluation of the molecular symmetry shows the two modes are of different symmetry.

## Internal Rotation of a Methyl Group

The internal rotation (or torsion) of a methyl group is one of the large-amplitude motions of chemical importance and the studies have been extended from microwave, Raman, and infrared spectroscopies to laser induced fluorescence excitation spectroscopy.[25-29] In the excitation studies, the supersonic expansion cooling technique has provided a powerful tool to study

the hindered internal rotation of methyl groups.[30,31] The internal rotation of a methyl group can show a strong dependence on electronic state. Spangler et al calculated the internal torsion barrier to be 28 $cm^{-1}$ in the ground state and 150 $cm^{-1}$ in the excited state for p-methyl-trans-stilbene by fitting the experiment results.[30]

The potential function for methyl internal rotation can be expressed by

$$V(\alpha) = \tfrac{1}{2}V_3(1-\cos3\alpha) + \tfrac{1}{2}V_6(1-\cos6\alpha) + \tfrac{1}{2}V_9(1-\cos\alpha) + \cdots \cdots$$

in which the $V_n$ are potential constants and $\alpha$ is the torsional angle. $V_3$ and $V_6$ terms are most often used to express the methyl torsion with higher terms rarely being needed. The first term in the potential function is dependent upon the symmetry, or the number of equivalent conformations. For example, in toluene, the methyl group has three equivalent hydrogens as has three fold symmetry and there is a two fold symmetry from the phenyl ring. Thus the total torsional potential in toluene has six minima.[31] The first no-zero term of the potential function determines the barrier height and higher order terms shape the potential. When the barrier height is zero, the energy levels associated with the torsion coincide with those of one-dimensional free rotor and are given by $Bm^2$. Here B is the internal rotation constant of the methyl group and m is the rotational angular momentum quantum number. When the torsional barrier is nonzero, the internal torsional levels become split by tunneling. The energy levels of a methyl rotor can be labeled by the internal rotation angular momentum number and the symmetry of the levels. The

levels are $0a_1$, $1e$, $2e$, $3a_2$, $3a_1$, $4e$, $5e$, $6a_2$, $6a_1$, ⋯ in order of increasing energy.[30] The above potential function can be used in the Hamiltonian to fit the observed methyl torsional transition frequencies.

If the methyl torsional transitions can be observed in a spectrum, the methyl rotor can be used as a probe to study electronic features of the molecule since it is very sensitive to the local electronic environment.[32]   A "remote" substitution effect can be delivered to the methyl rotor by a conjugated system, which is manifest as a change in torsional harrier with substitution.  Dorigo et al[34] found that hyperconjugation, the interaction between the p orbital of the carbon atom in the methyl rotor and the $\pi$ system, is the dominant influence on methyl behavior.  In aliphatic systems, the net hyperconjugation interaction is antibonding in the ground state and bonding in the excited state.  Therefore, the conformation of maximum overlap is favored in the excited state but not in the ground state.[30]

## Low Frequency Modes of Trans-Stilbenes

A number of groups have been involved in the study of trans-stilbene, however, many of them paid more attention to photoisomerization between trans and cis-stilbenes and the assignments of skeletal modes above $200$ cm$^{-1}$ instead of the low frequency ones.[35-40]  Warshel calculated the normal modes for $C_{2v}$ symmetry in both the ground and excited states using QCFF-$\pi$.[41]  Most of the later studies followed his notation to label the trans-stilbene modes.  The

observed low frequency modes in trans-stilbene have been assigned as $\nu_{25}$ (phenyl in-plane wag), $\nu_{37}$ (ring torsion), and $\nu_{36}$ (phenyl out-plane flap). The low frequency modes of $\nu_{25}$, $\nu_{37}$, and $\nu_{36}$ are $a_g$, $a_u$, and $a_u$ respectively. The totally symmetric mode $\nu_{25}$ has no restriction for the transitions between the $S_0$ and $S_1$ states. The $A_u$ modes, however, are restricted to only even quanta transitions. The transition frequencies of the three modes $25_0^1$, $37_0^2$, and $36_0^2$ in trans-stilbene were observed at 197.8, 95.3, and 69.6 cm$^{-1}$ in the excitation spectrum and at 200, 19.0 and 114 cm$^{-1}$ in the dispersed emission spectra, respectively.[42-44] Mode $\nu_{25}$ is harmonic in both ground and excited state but $\nu_{37}$ is only harmonic in the excited state. The very low first quanta and anharmonic potential of $\nu_{37}$ in the ground state and its strong couplings with other vibrational modes contribute to the acceleration of the intramolecular vibration redistribution rate.[45]

Some trans-stilbene van der Waals complexes and trans-stilbene-$H_2/D_2$ were studied by Zwier and co-workers.[46-48] They found a strong mode-dependent broadening of the van der Waals complex transitions associated with the low frequency vibration $37_0^2$.

## Ring Modes in Anilines

The assignments of the ring modes in aniline and its para-substituted analogs are based on the assignments of benzene[49,50] In each of the anilines the origin is prominent in its excitation spectrum. Only three benzene-like

ring modes appear with high intensities in the anilines, $\nu_{6a}$, $\nu_1$, and $\nu_{12}$, based on Wilson's classification for benzene[49]. All the three modes are totally symmetric. The transition frequencies of $6a_0^1$, $1_0^1$, and $12_0^1$ in the fluorescence excitation spectrum of aniline are at 493, 798, 954[4,10,13] respectively. Some disagreements for the assignments of mode $1_0^1$ and $12_0^1$ can be found in different publications. Brand, William, and Cook assigned the modes $12_0^1$ and $1_0^1$ for the peaks at 798 and 953 cm$^{-1}$, respectively. However the peaks at the above frequencies were assigned as $1_0^1$ and $12_0^1$ by Reilly and coworkers instead.[51] According to Varsanyi the $1_1$ has lower frequency than $12_1$ does in ground state.[50]

The absolute frequency of the origin is not certain even though it was shown to be around $34032 \pm 10$ cm$^{-1}$.[4,14] In the excitation spectra of para-substituted aniline (p-fluoroaniline and p-toluidine) the origin peaks shift down to 32658 and 33095 cm$^{-1}$ respectively according to Tembreull et al.[21] The $\nu_{6a}$ mode shifts down by about 60 cm$^{-1}$ but the other two ring modes $\nu_1$ and $\nu_{12}$ show only minor shift. This is because $\nu_{6a}$ involves some motion of the substituent.[49] Since all the three ring modes are totally symmetric, the transitions from these modes will have no restriction by the selection rules. All of the three modes in the anilines are nearly harmonic. The overtones should be easily found in the excitation spectra especially for the low frequency overtone $6a_0^2$.

In this thesis, we concentrate on the assignments for the internal modes in aniline and para substituted anilines in the FE and DE spectra.

# EXPERIMENTAL

## Fluorescence Excitation in a Supersonic Jet

A high power, frequency doubled, pulsed Nd: YAG (Lumonics HY750) was used to pump a tunable dye laser (Lumonics HyperDye 300) in the fluorescence excitation experiments. A 2400 groove/mm grating used at grazing incidence in the dye laser provides $0.07$ $cm^{-1}$ resolution. Since all the molecules discussed in this thesis involved $\pi \rightarrow \pi^*$ transitions located in the UV range, a dye laser frequency doubler (Lumonics HyperTrack 1000) was used to double the visible dye laser frequency to the UV.

All the laser dyes were purchased from Exciton. The sample was loaded in a stainless steel sample chamber and heated to increase the vapor pressure. High purity helium was allowed to flow over the sample, through a nozzle orifice (General Valve nozzle series-9 with 0.8 mm diameter), and then was expanded into the vacuum chamber.

The frequency doubled dye laser beam was passed through three apertures, which were used to exclude room light, then crossed the jet expansion at right angles. The intersection of the laser and jet axis was placed at the focal point of an ellipsoidal reflector (Melles Griot REM 014). Any emission was then

reflected to the second focal point where the photocathode of a photomultiplier tube (PMT, EMI 9813QB) was positioned. The resulting signal was measured by the PMT, amplified, and then sent to a boxcar averager (SRS boxcar system), digitized, and stored on an IBM compatible computer. The experimental set up is presented in Figure 2.

The supersonic expansion cooling is a thermodynamic process. The vibrational, rotational, and translational energies in a molecule are called thermoenergies because they are affected by temperature. However, only vibrational and rotational energies have significant effect on spectroscopy. These energies can be transferred by collision between molecules. When the molecules are passed through the nozzle orifice and expanded into the vacuum chamber, the collision between the sample molecules and the He atom will transfer the internal energy between the sample molecule to the atoms. In a gas phase mixture, the diluted sample molecules have much larger probability to collide with the carrier gas atoms than with themselves. Then the vibration and rotation energies will be transferred from the sample molecules to the carrier gas atoms since the collision is nonelastic. Finally the molecule can be cooled significantly. The temperature in the cooled sample molecules in the jet can be below 5 K, which is cold enough to cool all the sample molecules down to the zero quanta level in the ground state. Because the rotational levels are much lower energy than the vibrational levels, rotations cannot be completely cooled out. However, the lower the temperature, the less rotational levels will
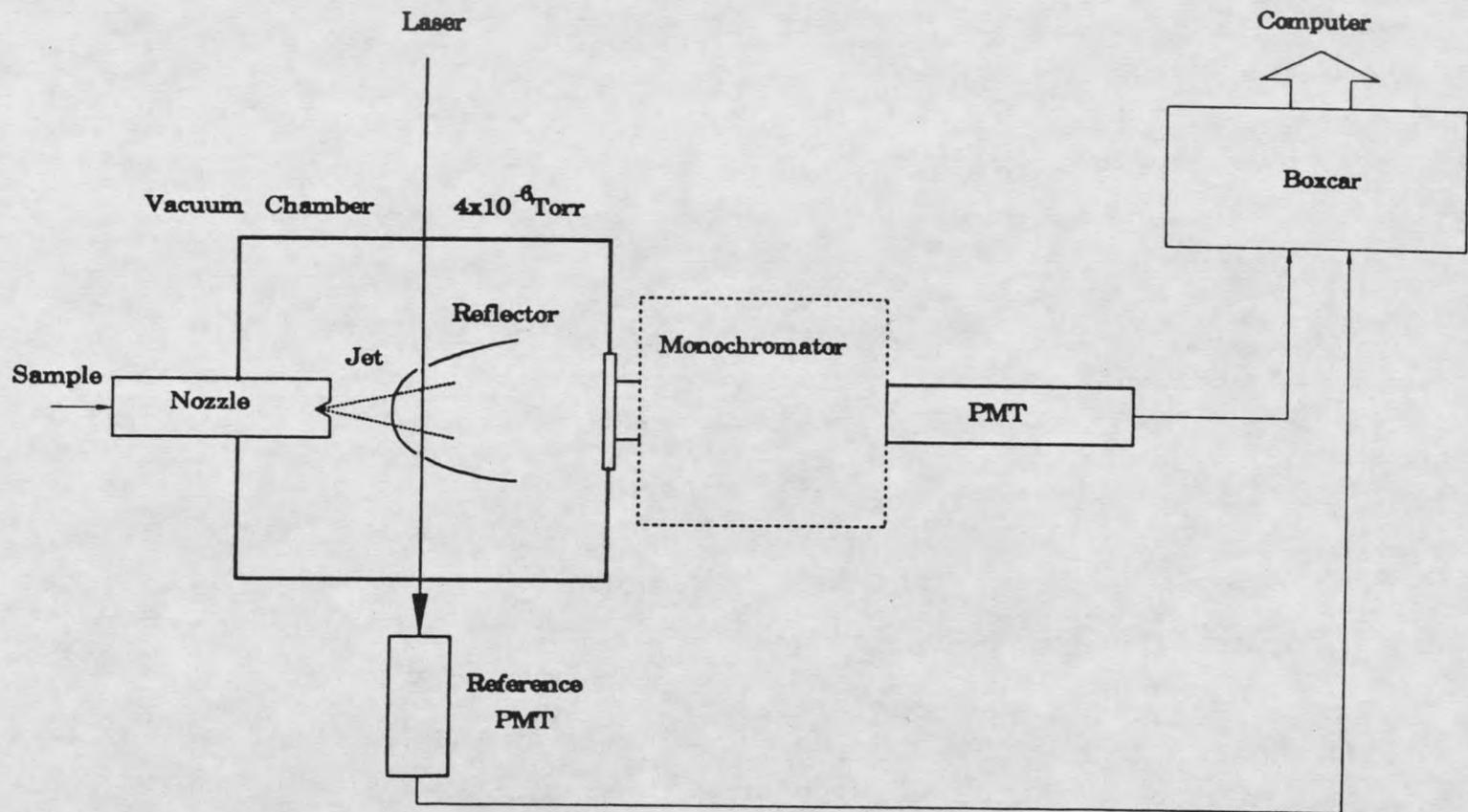
Figure 2.   The principle scheme of the experimental set up which is used for fluorescence excitation and dispersed emission experiment in a supersonic jet.

be populated, the narrower the observed band width will be in the excitation spectrum.

The expansion conditions can easily be changed by changing the He backing pressure over a range of 0.2 - 7 bar, gauge. High backing pressure makes the sample more dilute and the molecules have collisions with helium so that they are cooled more efficiently. At low backing pressure, however, the molecules cannot be cooled down to the zero vibrational level completely. Thus, some transitions will originate from the nonzero quanta in $S_0$ and are called hot bands in the excitation spectrum. Higher temperature will give hot bands more intensity in the spectrum which can aide in identification of same inversional bands. However, very high temperature can greatly complicate the spectrum due to the presence of numerous hot bands. Furthermore, the higher temperature will make the band width broader so that close transitions overlap. The temperatures for protonated and deuterated anilines at 7 bar of the backing pressure are predicted to about 5 K and 10.5 K respectively, according to the jet cooled spectra.

Another technique used in the fluorescence excitation experiment was to saturate the strong transition bands in order to get enough intensity in weak bands. In order to get a saturated spectrum, high laser power was used to excite the molecules which improved the signal to noise for the weak transitions.

## Dispersed Emission Technique

A fluorescence excitation spectrum of a cold molecule can provide very important information for the molecular behavior in an excited state. However, complete characterization requires probing the ground state as well. The fluorescence excitation and dispersed emission mechanism in a jet is presented in Figure 3. Assume all the transitions shown in Figure 3 are allowed. The molecules are pumped from the lowest level in the ground state to a single vibrational level in the excited state. When the molecular population is built up in the excited state, spontaneous emission will let the molecules lose energy and go down to the ground state. Fluorescence will be emitted in this process. Actually, not all the molecules will go back to the original level in the ground state. Some of the molecules will emit to different levels in the ground state.

It is equivalent to say that the fluorescence is composed of different frequencies, and if a monochromator is used, a dispersed emission spectrum can be obtained. The frequency difference from a transition to the origin band reveals the difference for the vibration levels.

In the dispersed emission set up, a monochromator is placed between the emitting molecule and the signal detector. At first the molecules were pumped from ground state to a certain level of the excited state. The emission signal, is then dispersed by the monochromator.
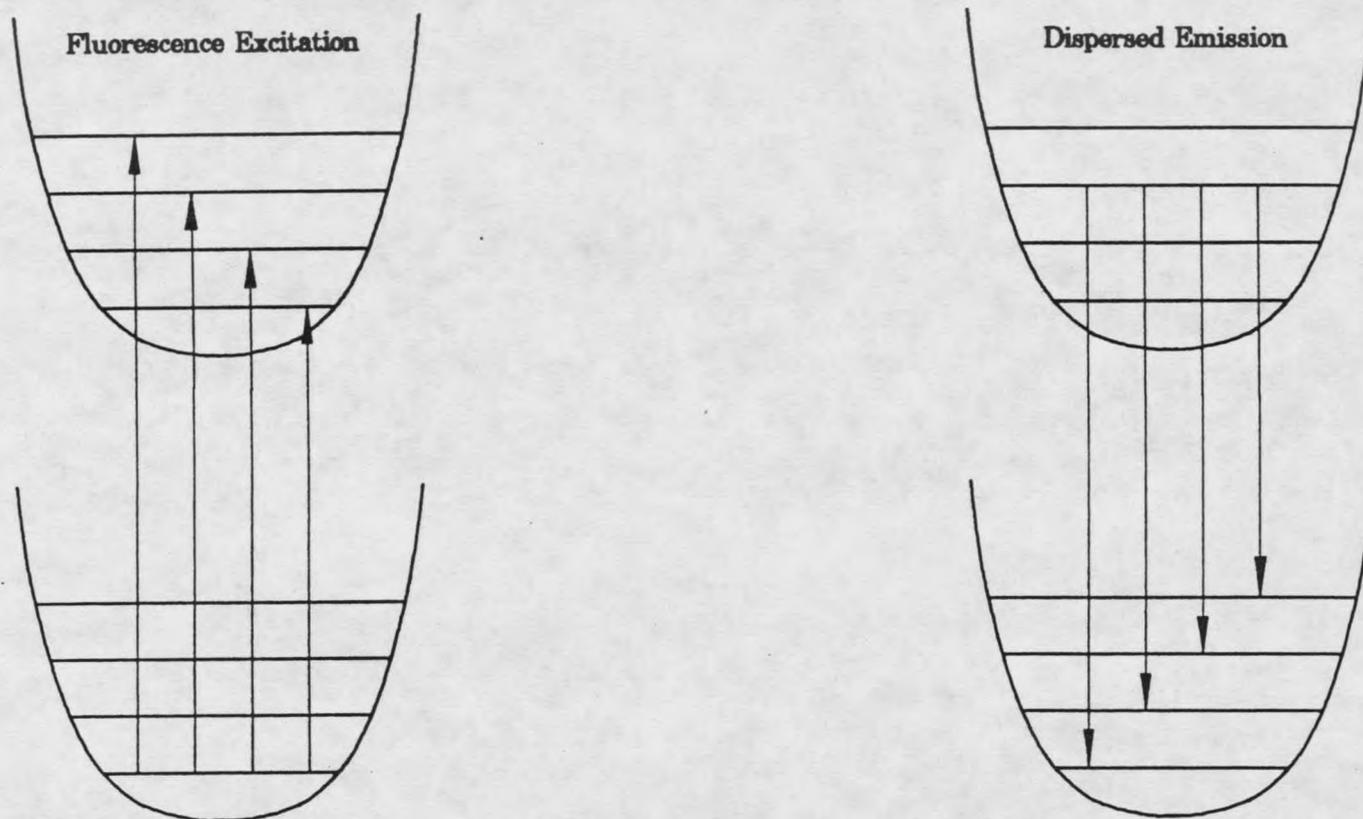
Figure 3. A diagram of the fluorescence excitation and dispersed emission processes. In the cold environment of the jet most absorptions originate in the v=0 level so fluorescence excitation probes the excited state. After pumping a selected level, ground state information can be obtained by dispersing the emission which terminates in multiple $S_0$ levels (right).

In the experiment, a quarter meter monochromator (ORIEL 77200) was used for the dispersed emission. The monochromator entrance slit was placed at the second focal point of the ellipsoidal reflector. The light was detected by a PMT and processed, digitalized and stored in the same fashion as the fluorescence excitation spectrum. The resolution of the monochromator ranged from 11 $cm^{-1}$ with 0.05 mm slit width to 22 $cm^{-1}$ with 0.1 mm slit width. Most of the dispersed emission spectra shown in this thesis were taken as an average of two scans and smoothed by 11 points.

## Materials

Aniline was obtained from Mallinckrodt Chemical Works and was used without further purification. Aniline-$ND_2$ was purchased from CIL with 99 percent purity claimed by the manufacturer, but both the excitation spectrum and NMR analysis showed the sample to be approximately 75 percent $ND_2$ and 25 percent NHD species. P-fluoroaniline and p-toluidine were purchased from Aldrich. The purities of p-fluoroaniline and p-toluidine were claimed by the manufacturer to be 99 percent and 99.9 percent, respectively, and were used in the experiments without further purification.

P-toluidine-$CD_3$ was made by Professor B. P. Mundy at Montana State University. The purity was shown to be about 90 percent by NMR and mass spectroscopy analysis.

P-toluidine-$ND_2$ was made from commercial p-toluidine by exchanging with