

Experimental Details

Molecular Beam Spectroscopy at St. Olaf College, Northfield, MN 55057

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Background

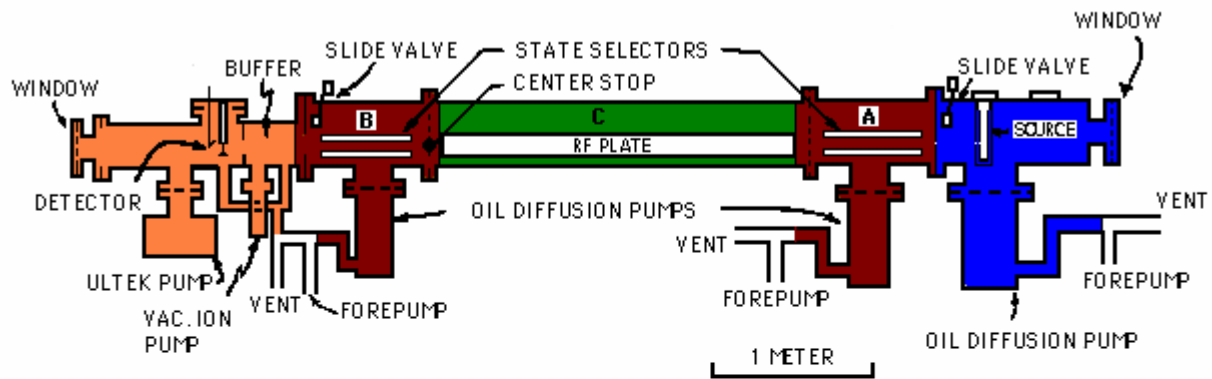
The molecular beam electric resonance spectrometer currently in use in the Physics Department at St. Olaf College was designed, built, and first used under the direction of Professor Norman Ramsey at Harvard University by Thomas Gallagher and Robert Hilborn, who used it as the basis for their 1971 PhD dissertations. Their work was published in *J. Chem. Phys.* **56**, 855-861 (1972) and *J. Chem. Phys.* **56**, 5972-5979 (1972). Subsequent Harvard dissertations using the same apparatus were completed by Joseph Cecchi (1972), Richard Freeman (1973), Abram Jacobson (1974), David Johnson (1975), James Byleckie (1979), and Dean Wilkening (1981). After the completion of Wilkening's experiment in 1981 the complete apparatus was moved to the Physics Department at St. Olaf College, Northfield, MN 55057, where it continued to be used by Professor (now emeritus) James Cederberg in collaboration with undergraduate physics students through 2009.

The most distinctive feature of the spectrometer is its 2.0 m long transition region which gives pure hyperfine linewidths of 100-200 Hz. In recent years we have developed computer software for the gathering of data with noise discrimination for signal averaging times of several days, making possible the observation of spectra even for heavy diatomic molecules with relatively large partition functions. Data analysis software has also been developed for fitting spectra to determine molecular parameters with higher precision than is currently possible in any other laboratories. Although other detector methods have been used, the current experiments all make use of a surface ionization ("hot wire") detector that is limited to easily ionized molecules, mainly those containing alkali atoms. The electrostatic quadrupole lenses used for state selection and focusing also limit the work to molecules with fairly large electric dipole moments.

I. Apparatus

A. Vacuum System

The overall vacuum system is 6.1 m long, containing five functional regions: Source (98 cm), "A" (64 cm, containing the first electrostatic quadrupole lens), "C" (280 cm, the transition region), "B" (69 cm, the second lens), and Detector (99 cm). Valves, operated by micrometer screws, separate the Source/A and B/Detector sections so that maintenance can be done on part of the system



without opening the whole to the atmosphere. A personal computer is dedicated to operating the diffusion pumps in the source, "A", and "B" regions. To provide protection against failures of the water cooling or the mechanical forepumps, it has a set of A-D converters in an interface to monitor the inlet and outlet water temperatures and the foreline thermocouple pressure gauges. Its D-A converters operate the relays that switch the diffusion pumps.

B. Source

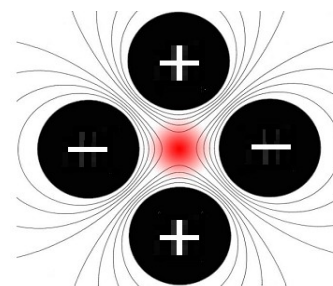
The source uses a design developed by Wilkening for his experiment on TLF. The sample is placed in a stainless steel tube 1.27 cm in diameter and 15.2 cm long, with welded end plugs. An effusive hole on the side of the oven that is 2-3 mm in diameter and about 8.2 cm from the bottom serves as the beam source. The oven is heated radiatively by passing a current through a concentric heater tube 1.9 cm in diameter, made from inconel foil rolled into a cylinder and spot welded. A copper frame supports the oven (mounted between Macor insulators) and carries the 60 Hz current to the ends of the heater tube. Around the oven assembly is a 7.6 cm diameter copper shield that is cooled by water through a soldered-on copper tube. A chromel-alumel thermocouple threaded through a small copper disk that rests in a recess at the top of the oven serves to give a temperature reading. The relatively large oven hole means that for most of the samples the desired beam flux is obtained at a temperature of 500-600 C, which is below the melting point. Sublimation from the solid grains seems to give a more stable beam than earlier designs that used smaller holes and temperatures above the melting point. It also means that the oven can be refilled by pouring the granular or powdered material in through the hole using a funnel made to fit around the oven tube. The effusive source does not give the rotational cooling that would be obtained with a jet nozzle, but it is simpler to maintain and gives a more predictable distribution of speeds and state populations in the beam. The source assembly with its cooled shield is mounted on a stainless steel bellows and a dove-tail flange that allows it to be moved vertically or horizontally for alignment. The current for the heater, typically 60-80 A, is provided via a step-down transformer powered by a variable autotransformer.

The source region is pumped by a 10 inch oil diffusion pump backed by a Welch mechanical pump. DC 705 silicone diffusion pump oil is used. Typical operating pressures, read by an ion gauge, for the source region are in the mid 10^{-7} Torr range, and are reached in about a day of pumping after closing the region following a reloading of the oven. Separating the chamber from the diffusion pump is a baffle that could be cooled with water or liquid nitrogen, but is left at ambient temperature. The chamber has a port where a second 10 inch diffusion pump could be attached if needed for gaseous jet sources, but is not currently used. Viton o-rings are used to seal the flanges of the chamber,

except for a window on the end that is sealed by a copper gasket. The entire top of the rectangular source section is a removable lid, also sealed with Viton o-rings.

C. Quadrupole Lenses

The "A" and "B" sections of the spectrometer each contain an electrostatic lens consisting of a set of four stainless steel rods 1.905 cm in diameter and about 43 cm long, aligned with their axes parallel to the beam line. The rods are supported with their axes on the vertices of a square, centered on the beam line, by Macor insulators, and connected electrically so that two opposite rods (top and bottom) are at a positive potential and the other two (left and right) negative.



Quadrupole lens array.

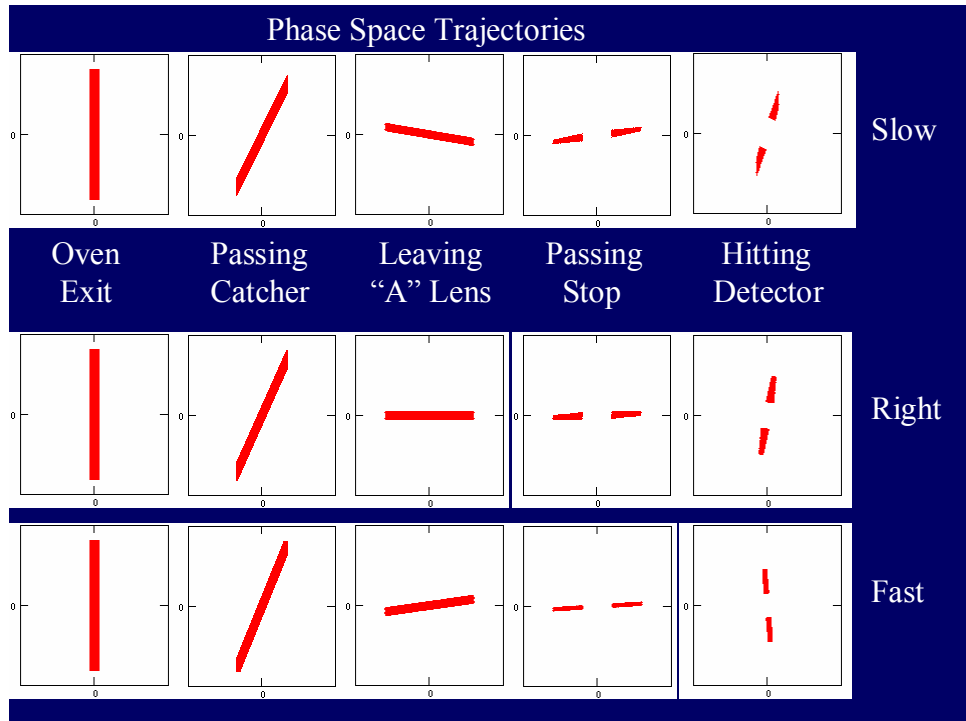
In this configuration they give a potential that is approximately of the form $V(x,y) = V_0*(y^2 - x^2)/a^2$, where a is the distance from the axis to the surface of each rod, and approximately also equal to the radius of each rod.

The more accurate treatment of the potential in the lens was described in *Am. J. Phys.* **58**, 257-261 (1990). With the approximate form, the corresponding electric field would be $\mathbf{E} = 2*V_0*(x \mathbf{i} - y \mathbf{j})/a^2$, and the square of its magnitude is $E^2 = 4*V_0^2*r^2/a^4$. This simple form, proportional to r^2 , combined with a molecular Stark energy proportional to E^2 , means that molecules in positively shifted states are subjected to a 2-dimensional harmonic potential. They would therefore undergo a harmonic oscillation about the beam axis with a frequency that depends on the Stark factor and the lens voltage V_0 . The goal is to set the lens voltage so that the desired molecules, starting on the axis at the oven, complete approximately one quarter of this harmonic oscillation by the time they exit the first lens, so that they are moving parallel to the beam axis. Molecules that happen to be in negatively-shifted Stark states will be pushed away from the axis and swept out of the beam. When the selected molecules in the parallel beam pass through the second lens, if no transition has occurred, they will complete another 1/4 cycle of the oscillation and converge in an image at the detector. If a transition is produced in the "C" region between the two lenses that takes some small fraction of the molecules into a state of different Stark energy, they will not converge to the detector and a drop in the detector signal results. The voltage applied to the lens rods is provided by a pair of 0-30kV Glassman power supplies, one for the positive and one for the negative, that are in turn controlled by a common 0-10V output of a D-A converter in the control computer.

Near the beginning of the second lens there is a beam stop that serves to block any molecules not deflected significantly by the lenses. Even when tuned for relatively high rotational states (we have made observations up to $J = 10$), the lenses will have little effect on molecules of still higher J , including most of the beam. Removing these molecules with the stop reduces the background statistical noise that they would contribute to the detector signal.

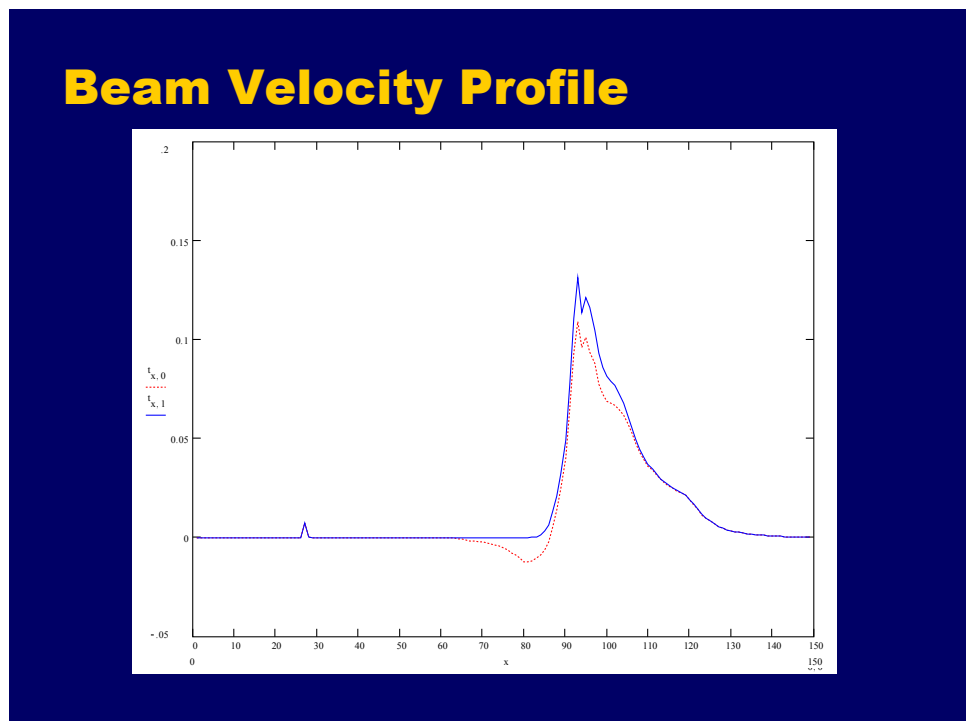
The more quantitative treatment of the lenses can be visualized by using a phase space representation of the molecular motions. Consider just one of the transverse dimensions. Position in this direction is the horizontal axis of the two-dimensional phase space, and the velocity in the same direction (appropriately scaled) is the vertical axis. Now consider a collection of molecules with the same speed along the beam axis as they leave the hole of the oven. The range of positions is limited by the size of the oven hole, but a

wide range of transverse velocities is possible. This is shown in the left-most frames of the figure. As these molecules move along the beam axis toward a cup with a hole that defines the beam, they also move transversely by an amount proportional to their transverse velocities. This is represented as a shearing in phase space, as shown in the second frames. The effect of the lens and the harmonic oscillation it produces is to rotate the figure in phase space. To get a parallel beam coming out of the lens we would need to



have the phase space figure rotate into a horizontal bar as shown in the third frame of the second row of the figure. Molecules with slightly lower velocities along the beam axis would rotate a bit too far, and those with slightly higher velocities would not rotate quite far enough, as shown in the top and bottom rows of the figure. Additional shearing would describe the motion through the transition region, and the beam stop clips out a slice in the middle, as shown in the fourth frames of each row. Finally, the second lens produces another rotation in phase space, and the width of the detector determines how many are detected.

By carrying out this process for a range of axial velocities, we obtain a velocity selection profile, as shown in the graph at right. The blue curve assumes that a transition has occurred to a defocused state such that no molecules are able to hit the detector. The



red curve assumes a transition to a state that is still focused but not as strongly.

The "A" and "B" sections are each pumped by a 6 inch oil diffusion pump, backed by a common Welch mechanical pump. Each pump also has a baffle separating it from the chamber, operated at ambient temperature. Each of the two sections has an ion gauge for monitoring the pressure, which typically runs in the mid 10^{-8} torr range. These pumps also maintain the vacuum in the "C" region, which does not have a separate pump. The "A", "B", and "C" sections of the vacuum chamber all have full-size rectangular lids, sealed with Viton o-rings, that allow easy access to the chambers.

D. Transition Region

The electric field that induces the quantum transitions in the beam molecules is produced by a pair of milled aluminum plates, 2.0 m long and about 10 cm high, separated by quartz spacers and held together by nylon bolts. Both rf and dc components are needed to produce the desired transitions.

The rf is produced by a Fluke 6060B synthesizer controlled via GPIB interfacing by the controlling computer, with a frequency referenced to an external Stanford Research Systems FS725 Rubidium Frequency Standard. From the Fluke the signal passes through a transistor switch and a broadband rf amplifier (Amplifier Research Model 15A250, 15 W, 10kHz-250MHz). The switch turns the rf on and off at about 11 Hz so that the control computer can find the change in detector signal due to the transitions by subtracting. The timing of this switching in the computer's interface board is also referenced to the synthesizer's frequency standard.

The dc component comes from a Kepko power supply controlled by a D-A signal from the controlling computer. The rf and dc signals are cabled separately to the vacuum flange at the top of the center of the "C" region, where they are coupled together by feeding the rf through a capacitor and the dc through an inductor to a single vacuum feedthrough. Inside the vacuum system a "T" splits this combined signal into two equal length lines, one going to the plates at 1/4 of their length, and the other at 3/4 of the length. Thus each half of the transition plates is center-fed by this pair of signals, hopefully reducing any standing wave effects. Since both the rf and dc are applied to the same plates, the two electric fields are parallel.

Because we are interested in seeing transitions at frequencies up to several tens of MHz, the lengths of the cables and the plates themselves can become significant compared to the signal wavelength. This means that there are standing wave effects that make the rf voltage applied to the plates different from that exiting the amplifier. In order to monitor these effects, an rf probe attached to the midpoint of the plates provides a dc signal proportional to the rf voltage.

In order to eliminate the effects of the Earth's magnetic field on the molecular spectra, the transition region is surrounded by a 35 cm diameter cylindrical magnetic shield of hipernom alloy. It is made in two halves for removal and access to the vacuum chamber. It is degaussed after assembly by passing a 60 Hz current of several hundred amperes through a single cable threaded through its length and slowly reducing the current to zero. We have a second, larger cylindrical shield that could be mounted outside the first, but, since its effect has been found to be negligible, it is not being used.

The transition region is designed to fit in the gap of a large electromagnet for study of Zeeman effects in the molecules. This was used by Cecchi and Freeman in their dissertations, but not in any subsequent experiments.

E. Detector

The detector filament used for molecules containing potassium, rubidium, or cesium is a ribbon of tantalum foil about 3 mm wide, mounted vertically and heated to bright orange by a dc current of about 3A. The work function of Ta is comparable to the ionization potentials of these elements (a bit over 4 V) so that a molecule landing on the heated filament leaves an electron behind when it evaporates away. The resulting ions are drawn to a metal collector mounted near the filament and maintained at a negative potential relative to the filament by a 9V battery. The current of ions is passed through a vacuum feedthrough to an FET op amp (AD 549JH) with a 10^8 ohm feedback resistor, so that a voltage of 1 V is obtained for an ion current of 10^{-8} A. This voltage is then passed to a voltage-to-frequency converter (Dynamic Measurements 8612) that produces a string of pulses at a rate proportional to the voltage in. These pulses are shaped by a Tektronix 114 pulse generator so that they can be dependably counted by the controlling computer. The width of the filament defines the horizontal sensitive area of the detector, while a horizontal slit in front of the filament defines the vertical dimension. Stainless steel bellows and micrometer screws allow for movement of the slit vertically and the filament horizontally to align it with the beam axis.

When running molecules containing Li or Na, the tantalum foil filament has been coated with tungsten by heating it in an evacuated bell jar containing an open vial of $W(CO)_6$. This volatile tungsten compound dissociates on contact with the hot Ta, leaving the pure W. Commercial tungsten foil has too much potassium impurity to be useable as a detector filament. To further increase the work function of the tungsten for detecting Li or Na, a stream of O_2 is played continuously onto the filament, raising the detector chamber pressure to 1-2 times 10^{-6} torr.

The detector section of the vacuum system is built with copper gasket seals so that it can be baked. This would be necessary if an electron bombardment detector were used, as it was for the experiment on ND3 at Harvard by Byleckie. In our recent use this has not been necessary, and the flange used to support the detector in the vacuum system is currently sealed by a Viton o-ring in place of the copper gasket for which it was intended. The vacuum is maintained by a pair of ion pumps, an Ultek 150 L/s directly under the detector, and a Varian 50 L/s in a buffer chamber between the "B" section and the main detector section. These typically operate in the mid 10^{-8} torr range. There is a sorption pump that can be used to get the pressure down far enough to get the ion pumps started, but we haven't used it. Instead we open a bakeable valve to the foreline to rough it out, then close that and open the beam-line valve to the "B" chamber to get the pressure down farther.

F. Data Collection

The spectrometer is controlled by a personal computer equipped with an interface board. The board includes the timing circuit for switching the rf on and off, the GPIB interface that communicates with the Fluke synthesizer and a Keithley digital voltmeter (for reading the oven temperature and rf amplitude), and four 0-10 V D-A output lines. One of these D-A lines controls the quadrupole lens power supplies, one the dc supply for the transition plates, one the 11 Hz square wave signal for switching the rf on and off, and one drives a relay to switch the Keithley between its two inputs.

To begin a run, the operator tells the computer the initial frequency, the frequency step size between bins, the number of bins, the number of sweeps through the frequency range, a phase shift between the switching of the rf and the reading of the detector, the quadrupole lens voltage, the rf amplitude, the dc transition voltage, and a file label designating the molecule. The phase shift setting is needed to account for the time it takes the molecules to get from the transition region to the detector, as well as any delay before the molecules re-evaporate as ions. This latter effect is dependent on the detector filament temperature. Typically the phase shift is set at about 30 degrees.

The computer then makes 10 measurements of the detector signal (by counting the pulses from the voltage-to-frequency converter) at the beginning frequency, to establish the statistical variation of the signal. It then steps through the frequency range, counting the pulses for rf off and rf on halves of the cycle and subtracting to get a difference. At each step it compares the rf-off count with the reference value from the initial calibration. If the current count is significantly different from the reference, it repeats the measurement at that frequency before stepping on. This catches most of the outliers due to pressure bursts from the diffusion pumps. The reference value is reset after each complete sweep to allow for slow drifts in the beam strength. After six sweeps, if more have been requested, the noise discrimination process changes. Up to this time all the separate rf-off and rf-on counts have been saved in memory. These values are then compared, and any outliers (counts greatly different from the others for that frequency bin) are removed. For subsequent sweeps the frequency is stepped without interruption, but any measurements for which the difference between rf-off and rf-on counts differs significantly from the average of previous sweeps are rejected. For each frequency bin two numbers are saved in memory: the total of all accepted count differences, and the number of accepted measurements. A graphical display is maintained on the computer monitor screen showing the average count difference per sweep as a function of frequency. The sweeps alternate in direction, so that odd-numbered sweeps step from low frequency to high, and the even-numbered ones from high to low. This should eliminate any systematic shifts due to delays from whatever cause. In the graph displayed on the screen the data points change color with the sweep direction, yellow if frequency is increasing, blue if decreasing, red if a point is rejected. When the run is completed, the data is written to both the computer hard drive and to a floppy drive that can be removed for analysis while the computer goes on to the next run. The conditions for several runs can be tabulated in a file on the floppy, so that the spectrometer can go from one run to another without human intervention. All of these features, plus some others that can be used for testing purposes, are programmed into an executable program we call "Winbeam.exe", whose source code is written in Visual c++ to take advantage of the Windows operating system.

II. Data Analysis

A. The Hamiltonian

Following a long tradition beginning with the invention of the molecular beam resonance technique by Rabi in the 1930s, we consider (along with the electronic, vibrational, and rotational terms) hyperfine effects that include nuclear electric quadrupole, spin-rotation, tensor and scalar spin-spin, magnetic octupole, and electric hexadecapole interactions, and also Stark energies due to external electric fields. Although the hyperfine effects are for the most part referenced to specific electronic, vibrational, and

rotational states, the nuclear quadrupole and Stark interactions do have non-zero matrix elements connecting different rotational states. Earlier molecular beam work generally dealt with these by using perturbation approximations, but the current availability of computers makes it easy for us to combine as many rotational states as needed into a single Hamiltonian matrix. We therefore find the elements of this matrix for each of the interactions, add them to the diagonal matrix of rotational energies, and use standard computer techniques to find the eigenvalues and eigenvectors at full machine precision. The expressions of Edmonds (*Angular Momentum in Quantum Mechanics*, Princeton University Press, Princeton, N.J., 1960) are used to express the matrix elements in terms of n-j functions and reduced matrix elements, and the reduced matrix elements are in turn expressed in terms of the standard spectroscopic parameters. Schlier (*Fortschr. Physik* **9**, 455-507 (1961)) showed how the parameters can depend on the specific vibrational and rotational state through a power series in the ratio of rotational constant to vibrational constant.

Our goal is to use our experimental measurements to determine better values for the hyperfine parameters as functions of vibration and rotation. This involves taking the best known or guessed values, finding the corresponding Hamiltonian matrix and its eigenvalues, and comparing the differences between the hyperfine states with our measured transition frequencies, and using a fitting procedure to adjust the parameter values. To get the transition frequencies from our data most precisely, we need to account for the Stark splittings of the lines, and that requires knowledge of the molecular parameters. This is a sort of boot-strap process of successive approximations that hopefully results in a consistent model of the molecule. We have developed two software fitting programs to do this. One, called "Linefit", fits our raw data to Stark-split resonances, and the other, called "Specfit", adjusts the molecular parameters to fit the frequencies determined by Linefit.

B. Specfit

This is a Mathcad worksheet that takes given initial guesses for the molecular parameters and sets up the Hamiltonian matrices, finds their eigenvalues and eigenvectors. If measured line frequencies are provided, it compares the eigenvalue differences with the measurements and then uses the singular value decomposition (SVD) method to determine the optimal parameters for fitting the data. It does this without consideration of Stark effects, so that the energies are independent of the quantum number M that describes the z component of the total angular momentum.

C. Linefit

This is an executable program we have written in c++ that uses the information generated in Specfit, adding the Stark term to the Hamiltonian, re-doing the eigenvalue calculation separately for each M state, and then combining this with the velocity-averaged Rabi lineshape function to get a Stark-split simulation of the spectrum. It compares this prediction with the experimental data for a run and uses a simplex method to fit it. The analysis of the quantum mechanics of the transition process, including the stark shifts, was worked out in *J. Mol. Spectrosc.* **166**, 158-168 (1994).

In running the program, the assumed line assignments for any lines in the data run would be specified. The program would calculate the frequencies, stark splittings, and velocity distribution, and an initial pre-fit would allow for the operator to make visual adjustments. The adjustable parameters include a background zero offset, the root frequency (before stark splitting) of each transition, an amplitude for each line (an option for separate amplitudes for

each stark component is provided), and five experimental "fudge factors". These fudge factors include:

1. An RF factor to take into account the fact that the rf voltage across the plates is not the same as that coming from the rf amplifier, because of standing wave effects. The factor depends on the frequency, and represents an effective ratio of the square root of the squared voltage averaged over the length of the plates to the millivolt rms output of the synthesizer (thus incorporating the gain of the amplifier, which is about 500). The rf probe mounted on the plates gives a rough indication of this value, but the observed stark splittings are used to refine it. We try to take a run of each line with the stark splittings dominated by the rf in order to give a value of the RF factor to use in other runs.

2. A DC factor that can be used to adjust the electric dipole moment of the molecule. The RF and DC factors are not directly fitted by the program, but are adjusted based on the fitted stark factor as described below.

3. A drive factor to correct for the fact that the effective average of the rf amplitude over the length of the plates is not necessarily the same as the rms average of the RF factor. The probability of transition depends on the product of the rf and dc fields, so what counts is the average amplitude of rf, since the dc should be uniform.

4. A time factor to tweak the velocity distribution calculated from using the phase space analysis of the quadrupole lens operation. In practice this never differs very much from unity, but can provide a slightly better match to observed linewidths in cases where the signal-to-noise ratio is particularly good.

5. A stark factor to match the observed stark splittings to the ones calculated from the fields and dipole moment. The stark shifts are determined by the sum of the squares of the dc and appropriately averaged rf fields. When possible we try to do at least two runs on each transition: one using large rf and weak dc fields from which we can get a good value of the RF factor, and a second with weak rf and strong dc from which we can find the root frequencies and, if not already known, a corrected value of the dipole moment. This means using the fitted stark factor for the rf-dominated run to find the RF factor, then using that to correct the dc-dominated fit. In the case of KBr the dipole moment and its dependence on vibration and rotation state was well known from other experiments, and ours simply confirmed this. For KI our results are more precise than previous ones and we include them in the publication. With the adjustments of RF factor and dipole moment, the stark factor in the fit is made to equal unity within its statistical uncertainty.

The root frequencies determined using Linefit are then entered into the data file used by Specfit to adjust the molecular parameters. If the changes are significant, Linefit would have to be rerun to take them into account.