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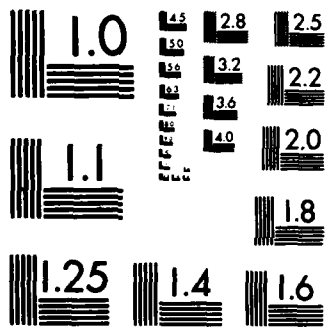
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INVERSION OF SPECTRAL LINESHAPES TO YIELD COLLISIONAL
RATE CONSTANTS

AD-A142 661

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State-to-State Transition Rates
Energy Corrected Sudden Scaling Theory

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

State-to-state collisional energy transfer rates are being obtained by the inversion of pressure broadened linewidth data. Measurements of linewidths in overtone vibration-rotation transitions have yielded information on rotationally elastic and inelastic collision rates for vibrationally excited HCl, HF, and CO. Similar information is being acquired for vibrationally excited DF. Work is continuing in evaluating the energy corrected sudden scaling theory.

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Table of Contents

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I. Background and Summary

Collisional interactions between molecules and molecular interactions with electromagnetic radiation are of essential importance to a large number of practical phenomena and devices. Much is known about the interaction of molecules in low levels of excitation. Because of the experimental difficulty in exciting molecules to higher levels, little is known about how the mechanisms of molecular interactions change with increasing vibrational excitation. Furthermore, little is known about how these interactions change with the temeprature of the system. However, it is just these rates for highly vibrationally excited molecules and high temperatures that are important in practical situations such as combustion, chemical laser devices, and the interaction of laser energy with matter.

When one attempts to model various practical phenomena an entire matrix of rotational and vibrational relaxation rates is required to include all of the relevant levels and interactions. Clearly the experimental observation of all these rates is a forbidding and probably impossible task. Furthermore, individual state-to-state rates are usually not measured even in the most sophisticated experiments and some relationship between rates is needed in order to interpret the experiment in terms of the collisional processes that participate in the observed parameter. This situation is further complicated by the fact that even if individual state-to-state rates are obtained, data must be provided over the temperature range that the particular device under consideration operates.

We have applied the Energy Corrected Sudden scaling approach to the inversion of pressure broadened linewidths to obtain rotational relaxation information.[1] The determination of any individual collisional transition rate

from a single bulk experiment such as pressure broadening has been considered difficult in the past because the pressure broadened linewidth is not very sensitive to any one component rate. In our approach to the inversion of linewidths to yield state-to-state rates, we are utilizing scaling relationships which fix the ratios of many rates within a family to a fundamental rate in that class, e.g. rotation-rotation or rotation-translation collisions. A small number of fundamental rates can then be determined by a small number of independent linewidth measurements with the scaling relationship providing the additional needed information. Also determined are dynamical factors which allow one to calculate the elastic contributions such as dephasing and the change in the various contributions to the linewidth with the vibrational excitation of the collision partners.

There are two specific advantages to acquiring state-to-state rates by the use of pressure broadening measurements. First, molecular beams or laser fluorescence experiments are amenable only to a small number of atoms or molecules. Spectroscopic measurements can be done on practically any species. Second, and most important, experiments that employ state-to-state pumping and subsequent detection of relaxation can only be employed for the lower vibrational levels of only a few molecules which have sufficiently strong overtone absorption cross sections. On the other hand, one can acquire simple absorption spectra for transitions to much higher states than would be feasible for these other techniques.

We have been successful in obtaining rotational-collisional transfer rates in a wide number of molecular systems such as HF, DF, HCl, and CO with various collision partners.[2-6] These studies have provided us with information about trends in collisional interactions as a function of the many parameters in these molecular systems, such as energy level spacings, dipole moments, mass, and polarizability.

II. Progress Report

During the first six months of this year's contract we have concentrated on acquiring spectroscopic data for deuterium fluoride to study its collision dynamics. We obtained spectra of the fundamental and first overtone bands with our Bomem Fourier Transform Infrared Spectrometer. Because of the fact that we were not sure that a commercial Fourier transform spectrometer would be capable of the accuracy required for these experiments we have had to perform a careful evaluation of the performance of the instrument during the data taking period. The pressure broadened linewidths which were obtained were inverted to yield rates for DF colliding with DF where one partner is in the $v = 0$ state and the other can be in the $v = 0$ through $v = 2$ state.

The original data which was used for developing and evaluating the ECS inversion approach was taken with the Kitt Peak National Observatory Fourier Transform Infrared Spectrograph. The Kitt Peak machine was chosen because it is the only instrument which we knew of that could give the proper fidelity of reproduction of the lineshapes to assure sufficiently accurate pressure broadening measurements.[5] Unfortunately we had only limited access to this machine. It became necessary for us to purchase an instrument that could match the performance of the Kitt Peak instrument or could be modified to do so. We chose the Bomem Inc. machine because we felt it had the best chance of being able to accomplish this. The Bomem machine was installed here and we found that when it was operated with the high resolution scanning heat it was incapable of the appropriate level of performance. It was found that this head was apparently damaged slightly in shipment and it has since been returned to the factory where it is being repaired. The company provided us with a lower resolution head which was sufficient for our preliminary work on

deuterium fluoride and we have used this to obtain the data reported below. A typical absorption line is shown in Figure 1. This is the P(5) line of the fundamental rotation-vibration band of DF. This spectrum was taken with a 1 mm pathlength absorption cell at room temperature. The crosses marked in the spectrum are the actual spectrum and the line is the best fit to this spectrum of a Voigt profile, which is generated by our nonlinear least squares fitting routine. As you can see the line is quite symmetric and fits the Voigt profile well. Our experience with commercial spectrographs in the past has been that this performance was very difficult to obtain. We are quite satisfied now that we will be able to continue our work with this machine in the future.

One thing which we will be able to do with our inversion procedure is to obtain linewidth data for transitions arising from very high j states. Figure 2 shows a spectrum which was taken in the R branch of the fundamental absorption band showing lines arising from states as high as $j = 13$. This is simply done by using a very long path absorption cell which makes it possible to see these very weak absorptions. Unfortunately the pressure broadening coefficient for these lines is exceedingly small and it will require that the high resolution head be reinstalled in order to be able to obtain data for these states.

Figure 3 shows the measured pressure broadening coefficient which we obtained for the fundamental and first overtone bands of DF. At the resolution we have available to us now, we can obtain data for lines arising from rotational states up to $j = 8$. You can see that there is only a very slight difference in the pressure broadening coefficients in the 1-0 and 2-0 bands indicating that there is only a small change in collision dynamics for DF molecules from $v = 0$ up to $v = 2$. We inverted this data utilizing the ECS inversion procedure and obtained state-to-state rotational relaxation rates

for DF colliding with DF for $v = 0$ through $v = 2$. As you might expect the behavior which we observe in DF is similar to that that we have observed in HF as reported in a previous paper. First, we find that rotation-rotation energy transfer collisions are the predominant relaxation mechanism in this molecule and, second, that energetic considerations are the most important in determining which collisions are most favorable. We found that this is generally true in HF and HCl in contrast to CO where the rotational energy level spacing is small compared to kT.[3,4,6] As an example of the behavior of DF, we show the rotational to translational energy transfer rates in various states for collisions in which the rotational state changes by $\Delta J = -1$. We see that the rotational translation energy transfer rates decrease as the rotational state of the molecule increases and this appears to be due to the fact that the energy level spacing of the molecules increases as 2BJ, and therefore the energy defect for the collision becomes much greater. We also note that there is little change in the collision cross sections for molecules in $v = 1$ and $v = 2$ as can be seen from the very slight difference in the pressure broadening coefficients for the fundamental and first overtone bands.

We note in examining Figure 3 that the linewidth in the P and R branch of the DF absorptions in both the 1-0 and 2-0 band are slightly different. This has been noted before in HF and HCl.[3,4] We see that the fitting procedure does not reproduce this asymmetry. This error is on the 10% level and produces a negligible effect in the reported rotation-rotation energy transfer rates which are the major contributing processes to the pressure broadened linewidths. However, this does result in more substantial errors to the reported values of the minor contributors to the linewidths such as multi-quanta energy transfer collisions. We have been carefully examining this effect. One of the reasons that we studied the CO system was to see if this

could be observed in a molecule which has much different properties than the hydrogen halides and we found that it did not occur in this system up to $v = 3$. We feel that this effect is due to the elastic collision component of the linewidth which begins to become more prominent as the intermolecular potential between the collision partners changes when one of the collision partners becomes vibrationally excited. It seems that the ECS scaling theory does not properly handle the elastic collision components of the linewidth. This may be due to the fact that the S-matrix in the ECS scaling formalism is not unitary. Because of this we have begun thinking about new ways to express these scaling relations which might avoid these problems. As part of our program, we have begun to investigate the use of the exponential distorted wave approximation as another way to express scaling relationships between S-matrices. This is presently underway as part of the theoretical program conducted by Herschel Rabitz. When a usable set of scaling relations is derived we will evaluate this new approach as part of this program.

We are continuing our attempt to acquire pressure broadening data for the 5-0 overtone band of DF with out laser photoacoustic spectrometer. The problem that still remains is how best to use the photoacoustic technique with very corrosive gases. Some considerable progress was made last year in understanding corrosion processes in the microphones that we use, and we have recently assembled an all teflon cell utilizing microphones that are potted in halocarbon wax.

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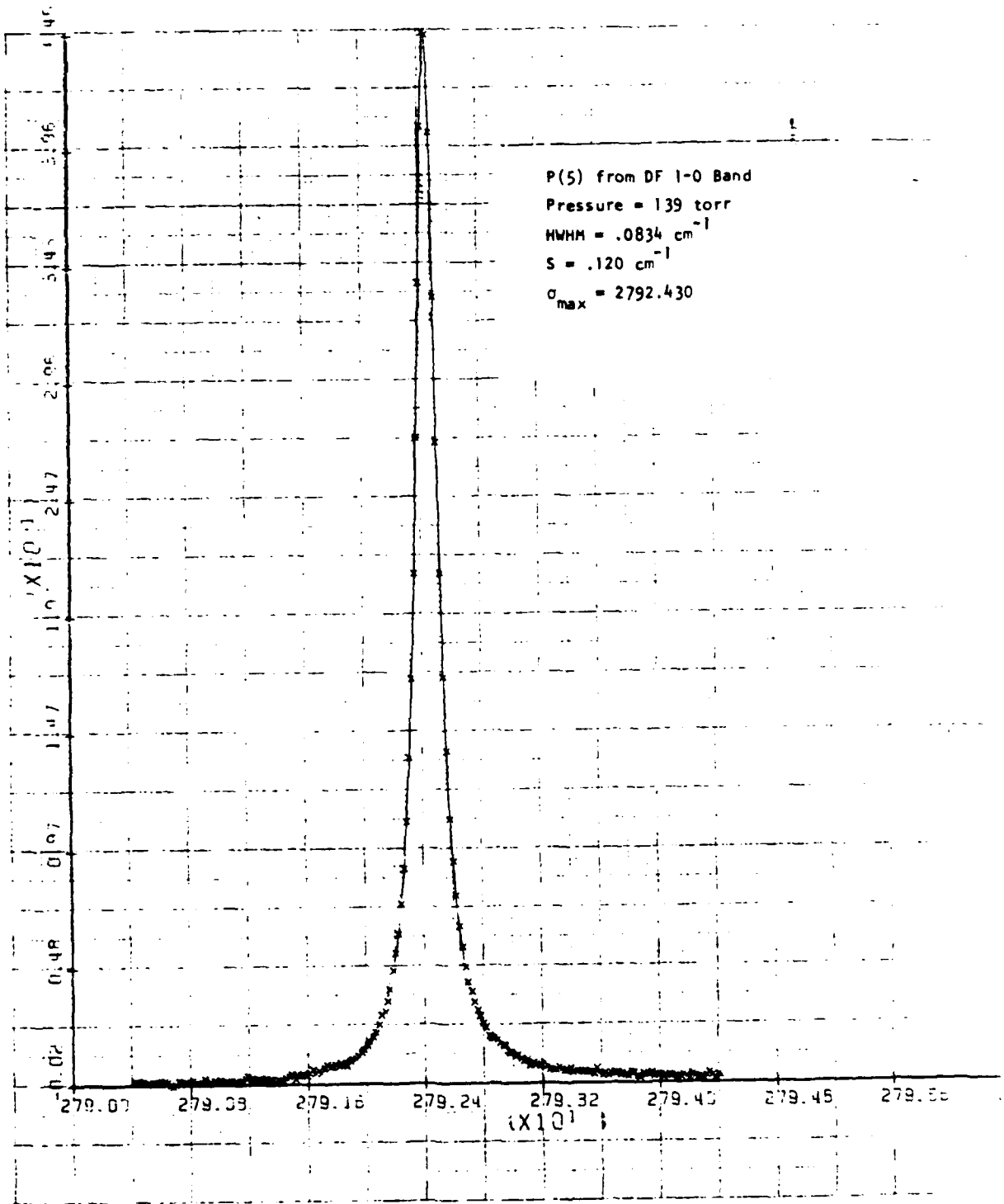
Figure 1. Typical spectral line and fit to a voigt profile (solid line).
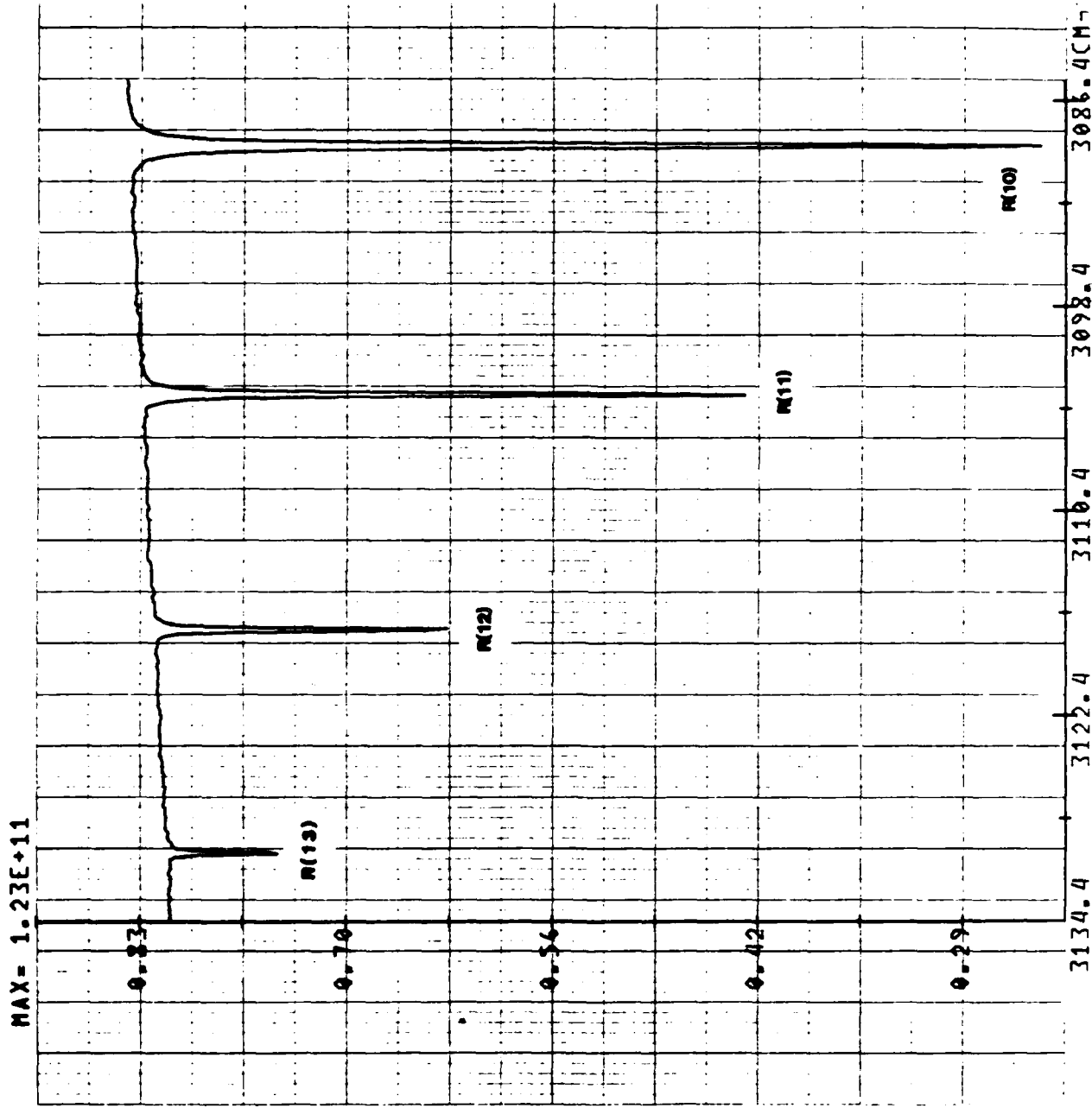
Figure 2. Absorption spectrum of a portion of the fundamental rotation-vibration band of DF showing the R(10) through R(13) transitions.
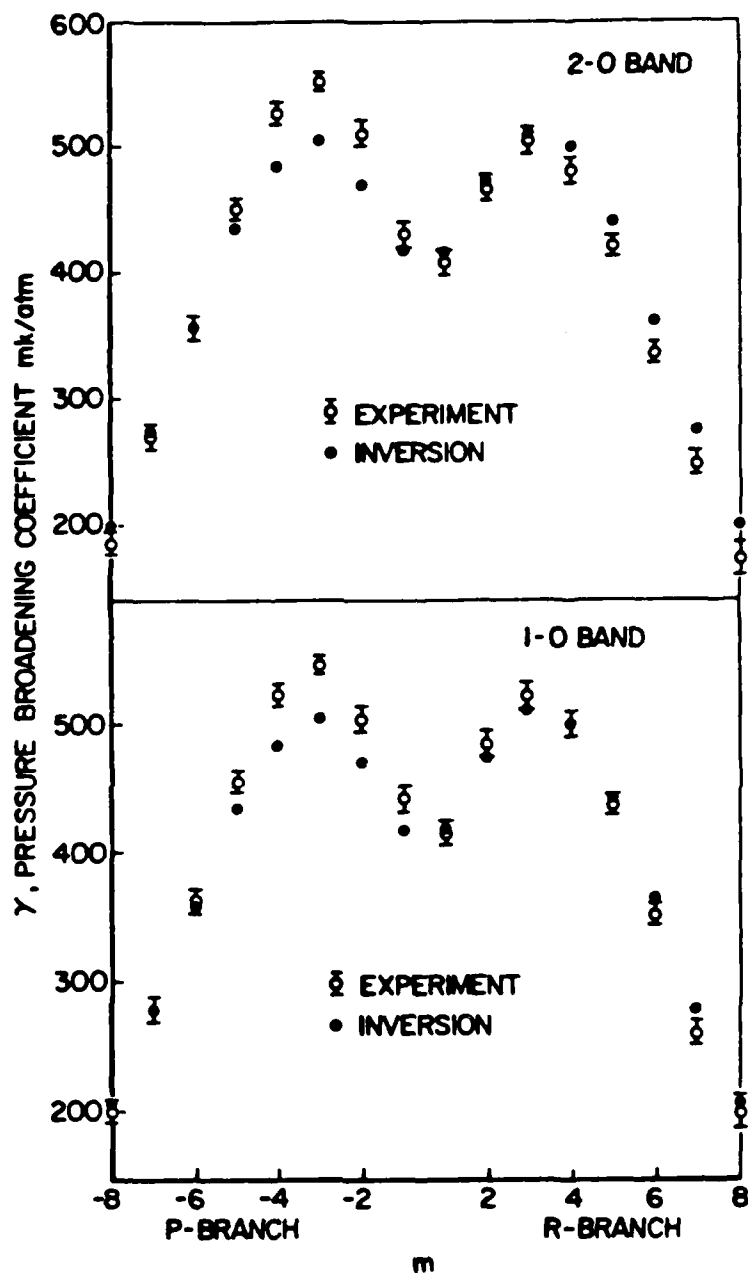
Figure 3. Pressure broadening coefficient, γ, for pure DF for the 1-0 and
2-0 bands. The points labelled inversion are computed from the
fundamental rates and dynamical factors extracted from the
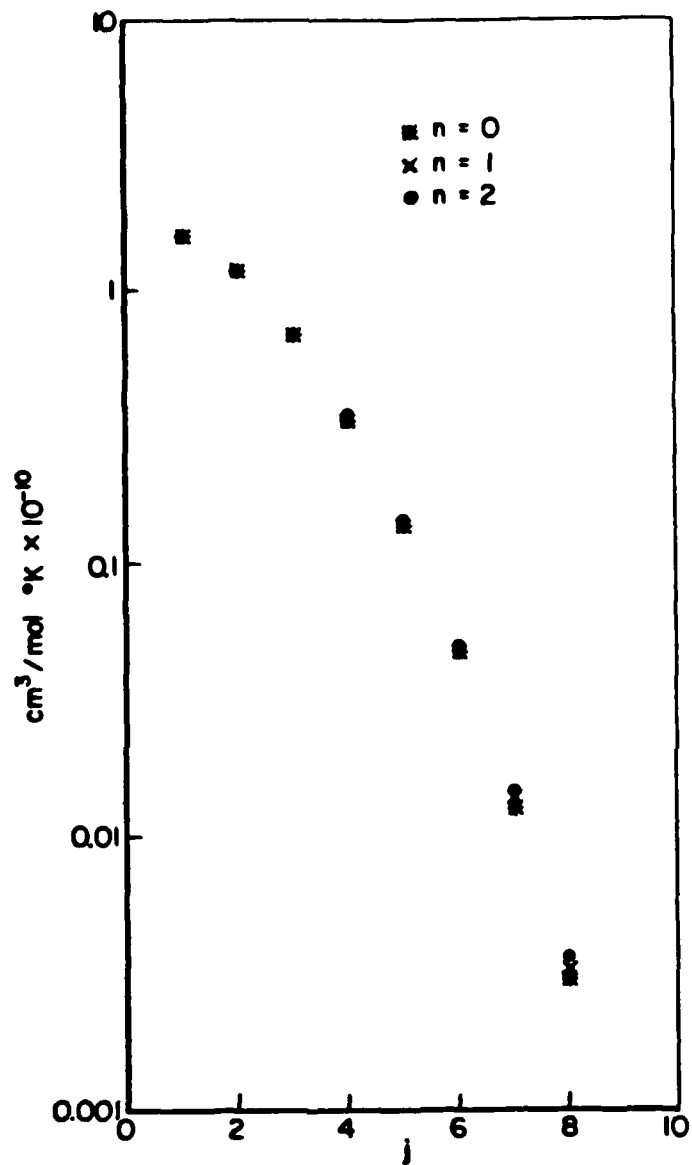inversion procedure.

Figure 4. Rotational-translational rates, $k(j \rightarrow j-1)$ for molecules in $V=0$, $V=1$ and $V=2$ colliding with ground state molecules.

III. Publications During the Term of this Contract

1. J. BelBruno, J. Gelfand, W. Radigan and D. Mitze, "Line Strengths in the First and Second Overtone Bands of Carbon Monoxide", J. Mol. Spec. submitted (1984).

2. J. BelBruno, J. Gelfand and H. Rabitz, "Collision Dynamical Information from Pressure Broadening: Application to Carbon Monoxide," J. Chem. Phys. 78, 3990 (1983).

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6. E. Wilczek, J. BelBruno and J. Gelfand, "Voigt Profiles of Spectral Lines: Accuracy of Line Parameters as a Function of Peak Transmittance," Appl. Spectroscopy 35, 443 (1981).

IV. Graduate Students and Postdoctoral Personnel

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8