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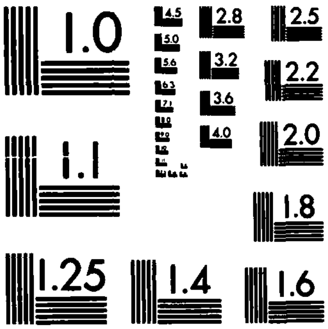

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Report Number 3

INVERSION OF SPECTRAL LINESHAPES TO YIELD COLLISIONAL RATE CONSTANTS

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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

I. Background and Summary

Collisional interactions between molecules, and molecular interactions with infrared and visible radiation are of essential importance to a large number of practical phenomena and devices. Much is known about the interactions 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 interaction change with increasing vibrational excitation. However, it is just these rates for highly vibrationally excited molecules that are important in practical situations such as high temperature environments, combustion gases, chemical laser devices and interaction of laser energy with matter.

An exact model for these various phenomena would require an entire matrix of rotational relaxation rates of the order of 10^2 to 10^3 to include all of the relevant levels and interactions. Clearly, the experimental observations of all of these rates is a forbidding and probably impossible task. We have applied the energy corrected sudden (ECS) scaling approach to the inversion of pressure broadened linewidths to obtain this information.[1] The determination of any individual collision 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 fit the ratio of many rates within a family to a fundamental rate in that class, e.g. rotation-rotation or rotation-translation collision. A small number of fundamental rates can then be determined by a small number of independent linewidth measurements. 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 partner.

We have been successful in obtaining rotational-collisional transfer rates in a wide number of molecular systems such as HF, 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. This wide range of information is providing us with an assessment of the use of scaling relationships in collision dynamics. 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 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. One can acquire simple absorption spectra for transitions to much higher states than would be feasible for these other techniques.

II. Progress Report

Work is continuing on obtaining state-to-state rotational relaxation rates for deuterium fluoride in the ground and excited vibrational states. We have installed a Bomem Fourier Transform Infrared Spectrometer which will be used to obtain spectra in the fundamental and lower overtone vibration-rotation bands of DF. A portion of the 2-0 first overtone band of DF which was obtained with this instrument is shown in Figure 1. This is a room temperature spectrum taken with a 1 cm path length monel absorption cell. We are presently working on acquiring spectra in the fundamental 2-0 and 3-0 bands for pure DF, DF-rare gas and DF-N_2. We are also working on obtaining spectra for the higher overtone bands at visible wavelengths with our laser photoacoustic spectrometer. Figure 2 shows a portion of the 6-0 overtone band of HCl taken with our laser photoacoustic spectrometer. This band is in the same region as the 6-0 band of DF. We are still having some difficulty with corrosion in the laser photoacoustic system in the presence of DF. During the past year we have spent some time learning to make our own corrosion resistant microphones and we will be in a position to obtain DF spectra of the same quality as the HCl spectrum shown in the near future.

We have obtained data for CO-CO and CO-He systems.[5] In addition, utilizing data from the literature, we have produced a general analysis of the effect of collision partners in the CO-X (X = CO, He, Ne, Ar, Xe, H) system.[6] Comparisons have been made with available double resonance experiments and theoretical calculations in the literature.

We found in our previous work on HCl and HF that the large dipole moments of these molecules lead to HX-HX collisions in which long range attraction is the dominant force.[2-4] The small dipole moment of CO lessens this effect and the expectation is that short range forces may become more important. This would be obviously true for rare gas-CO collisions. Furthermore, the harmonic potential well and small vibration-rotation interactions would lead one to believe that there is only a small dependence of the rotational collision dynamics on vibrational excitation in contrast to that found in HCl and HF.

The 2-0 and 3-0 bands of carbon monoxide and carbon monoxide diluted in helium were recorded at Kitt Peak National Observatory. Pressure broadening coefficients for the rare gases other than helium were taken from the work of Bouanich.[7] The CO-H_2 broadening data are the results of Nerf and Sonnenberg.[8] The linewidths in the CO-CO and CO-He systems for the overtones that were studied are presented in Figures 3 and 4. The literature values for the fundamental transitions in the CO-He system fron Benedict et. al. are also given.[9] The 1-0 band data for pure CO is not shown because the several reported measurements differ by as much as 30%. (The data we obtained in the overtone bands are considerably more accurate than that which is available for the fundamental band in the literature.) First we note that there is no observable change in the pressure broadening coefficients for the different overtone bands in both systems. As is expected, this is in contrast to the HCl and HF data which we have previously studied and indicates that up to $v = 3$ there is no observable change in the rotational collision dynamics of CO molecules.

We also note that the self- and helium-broadened widths exhibit two distinctly different types of behavior in the plots of width versus the rotational quantum number of the spectroscopic transition. This is indicative of the difference in the collision dynamics of the two different collision partners. In pure carbon monoxide there is a monotonic decrease of the pressure broadening coefficients with increasing j. This is characteristic of a system dominated by R-T energy transfer collisions. A decrease in the efficiency of R-T energy transfer is expected with increasing j, since the amount of energy transfer to translation increases approximately as 2Bj. The helium broadened linewidths are essentially independent of j. This is indicative of a fundamentally different behavior for the R-T collision processes with helium. In particular the monotonically decreasing R-T rate constants as a function of the j state of the collision partners could not produce the curve shown in Figure 4. Rather it is required that there be a peak in the R-T rate constants at some intermediate value of j to reproduce the data shown.

Some illustrative rate constants in CO-CO and CO-He systems are shown in Figures 5 and 6. The rate constants for the small Δj collisional transitions in pure CO are 2 to 10 times larger than the corresponding values in the CO-He mixtures. This accounts for the larger pressure broadening coefficients in pure CO. We note, however, for collisions where there are large Δj changes the rate constants in helium are significantly greater than those in the pure gas. This increased significance of multi-quanta transitions in CO-He collisions may be attributed to the more sudden nature of that collision; the transfer of large amounts of energy should be relatively more efficient for the harder CO-He collisions. We note the pattern of the shifting of the j value for the most probable collision in CO-He. When taken with the similar pattern in de-excitation collisions this appears to lead to the very small dependence of the linewidth on transition number in the band that we have observed. Also note that for the $\Delta j = 1$ R-T excitation collisions in pure CO there is a small peak in the rate of molecules in $j = 2$. This was apparent in both the HCl and HF systems as well. This behavior has also been observed in beam experiments in HF.[9]

A great deal can be learned about trends in collision dynamics with various collision partners by studying pressure broadening in mixed systems. A qualitative classification is apparent in the available data for CO diluted in H_2, He, Ne, Ar, and Xe. The pressure broadening coefficients indicate that the collision dynamics of CO with CO, Xe, or Ar are similar, and are clearly distinguishable as a separate class from the other collision partners. The behavior of Ne as the perturbing atom is intermediate in nature. There are two dominant trends apparent in this information. As the molecular weight of the inert gas increases, the rate constants take on the characteristics of those shown by collisions between CO and CO. The collision dynamics of the lighter gases are dominated by their higher velocities and consequently more sudden collisions. The heavier gases are dominated by their slower velocity and substantial polarizability which leads to a longer range attraction hence more adiabatic collisions. This observed behavior is very similar to that reported by Oka for ammonia with various collision partners.[10] We see in this study the power of the scaling theory approach to these collision dynamics problems providing the large amount of data for many systems from easily obtainable pressure broadening measurements. A more complete discussion of the points given here is presented in reference 6.

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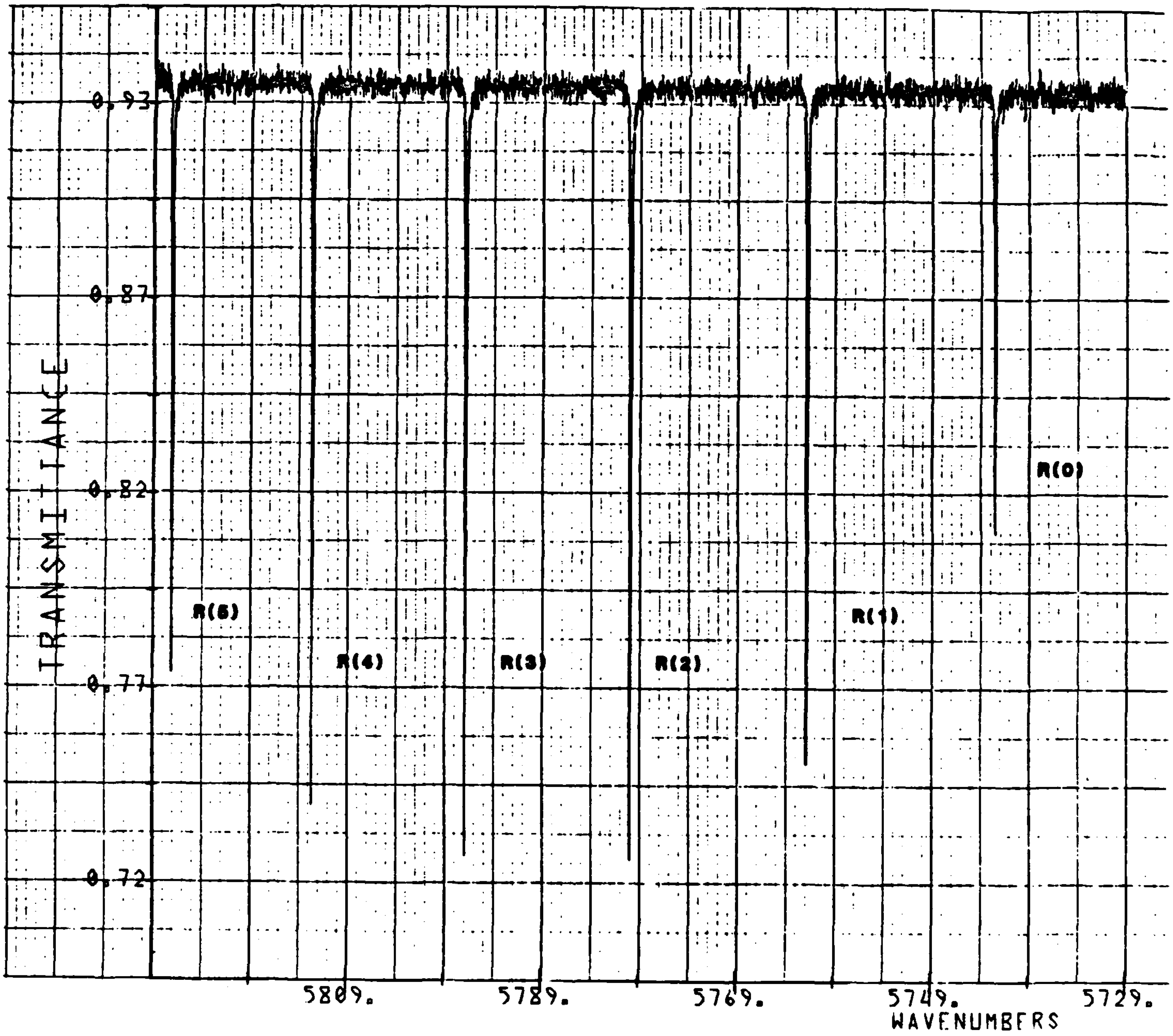

Figure 1. Absorption spectrum of a portion of the R-branch of the 2-0 overtone spectrum of DF. This spectrum was taken at 180 torr of pure DF with a 1 cm pathlength and a resolution of 0.033 cm^{-1}.

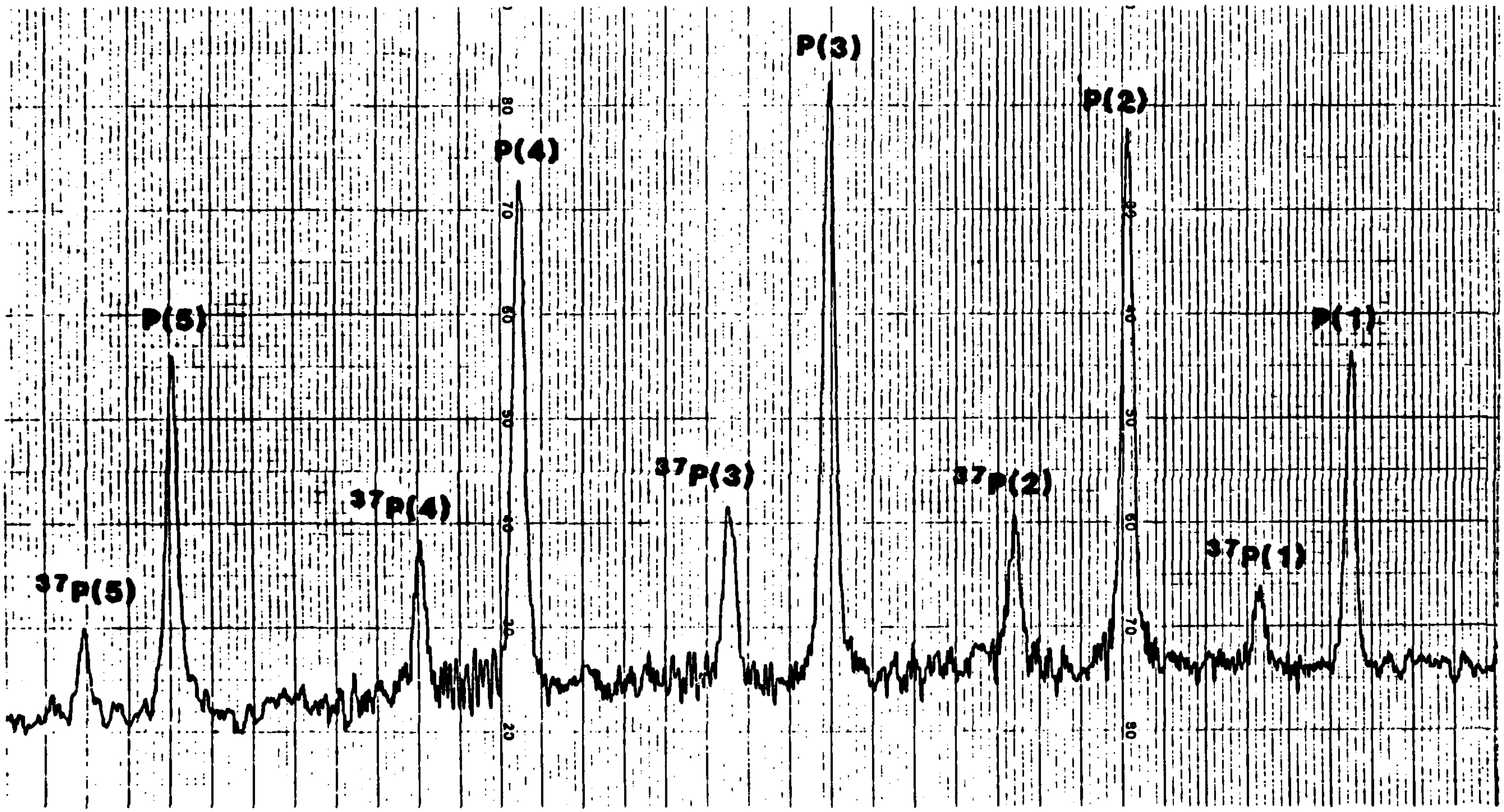

Figure 2. Laser photoacoustic spectrum of a portion of the 6-0 overtone band of HCl in the region of 6350Å. Transitions for the $H^{35}Cl$ and $H^{37}Cl$ isotopic species are shown.

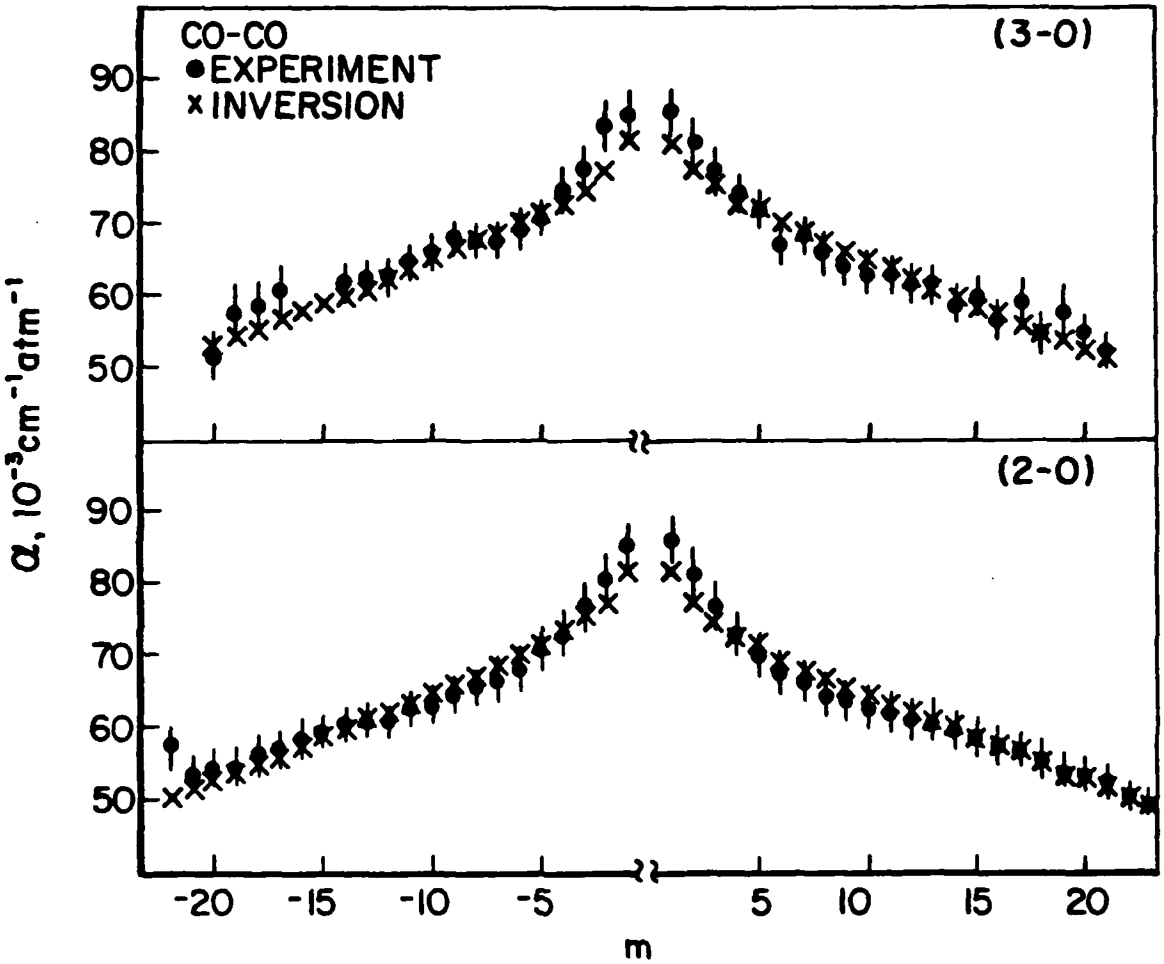

Figure 3. Pressure broadening coefficient, α, for pure CO for the 2-0 and 3-0 overtone band. The points labelled inversion are computed from the fundamental rates and dynamical factors extracted from the inversion procedure.

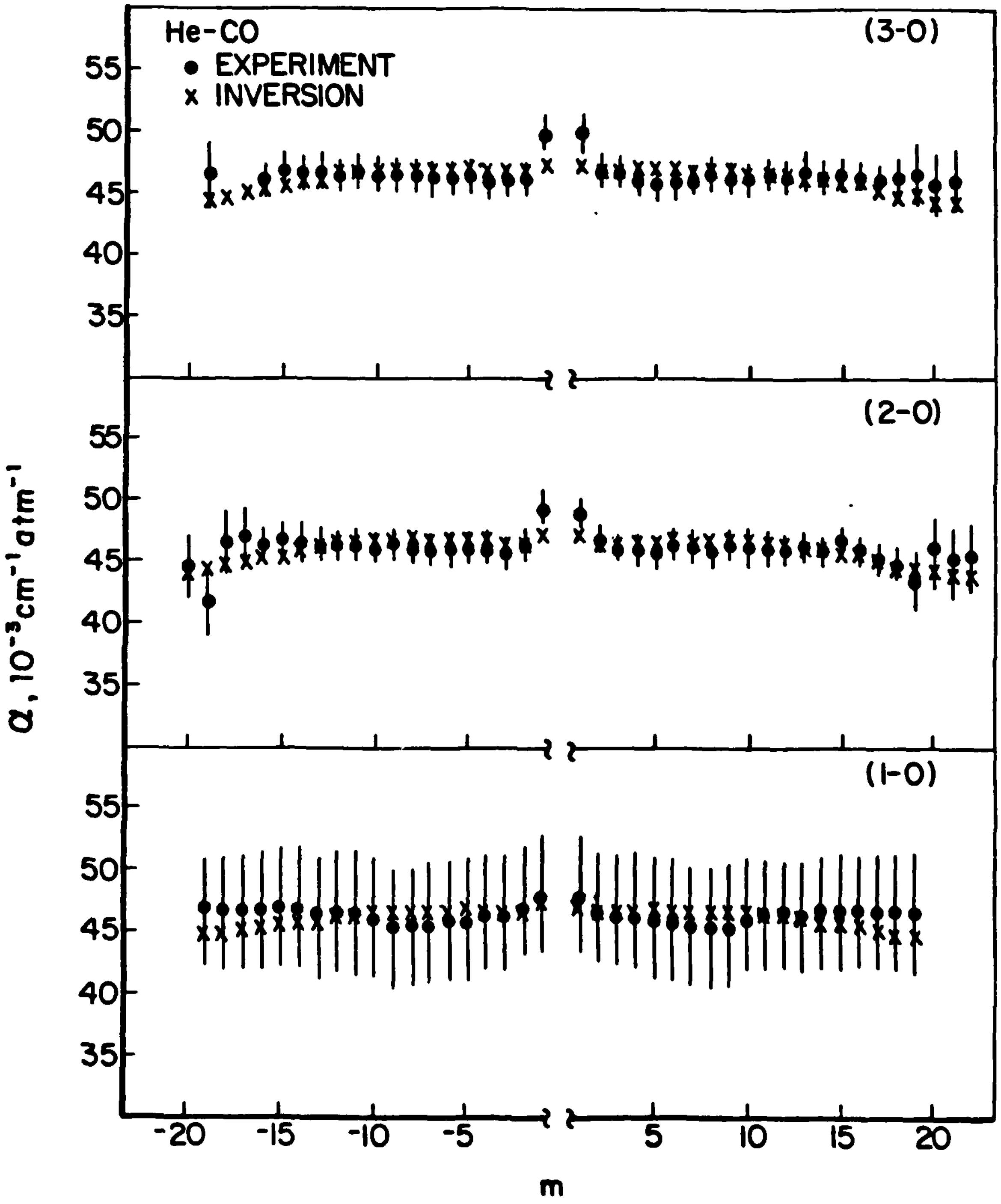

Figure 4. Pressure broadening coefficient, α, for CO broadened by He for the fundamental and the 2-0 and 3-0 overtone bands. The points labelled inversion are computed from the fundamental rates and dynamical factors extracted from the inversion procedure.

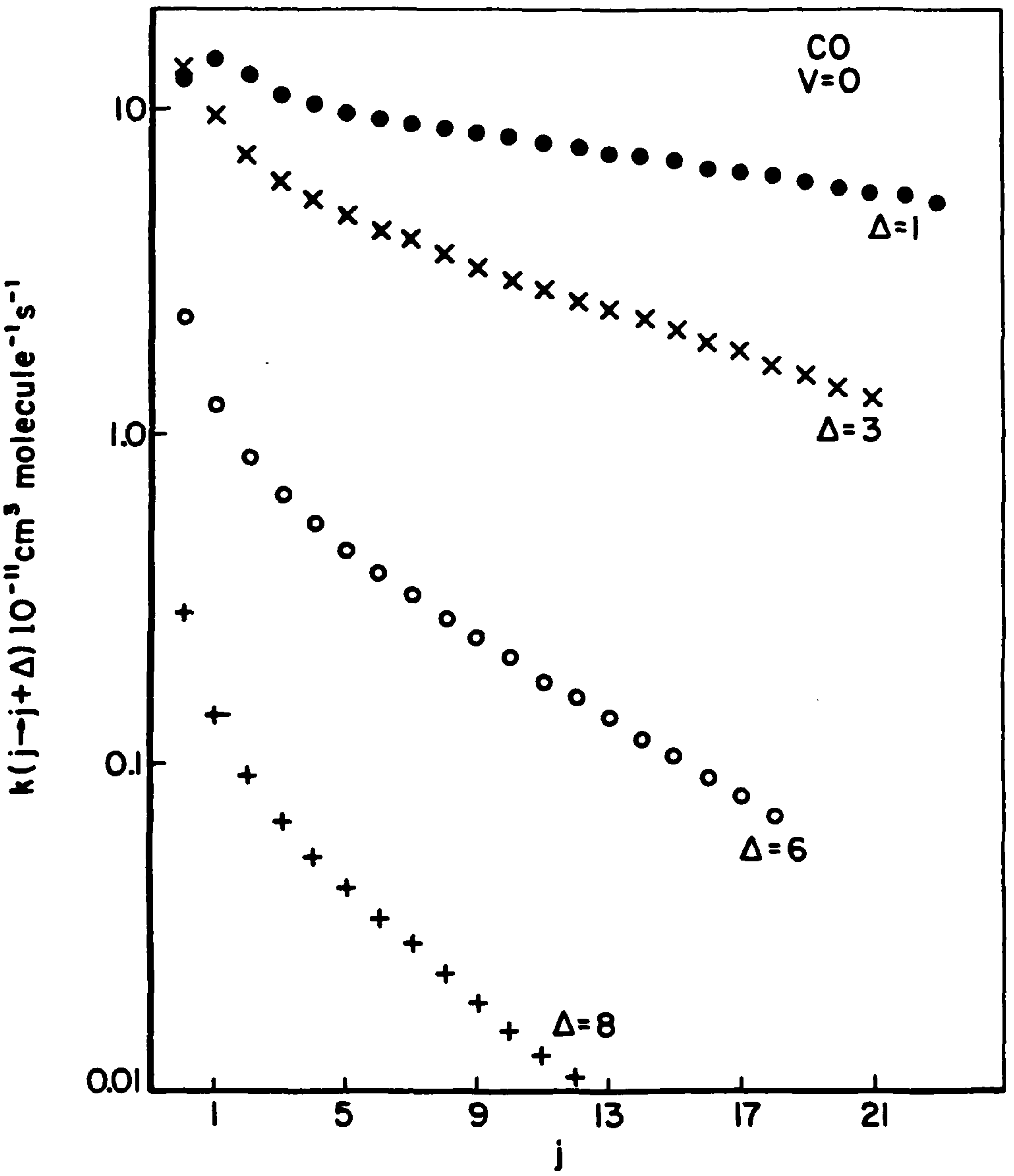

Figure 5. Single and multi-quanta R-T collisional excitation rate constants for CO in V = 0.

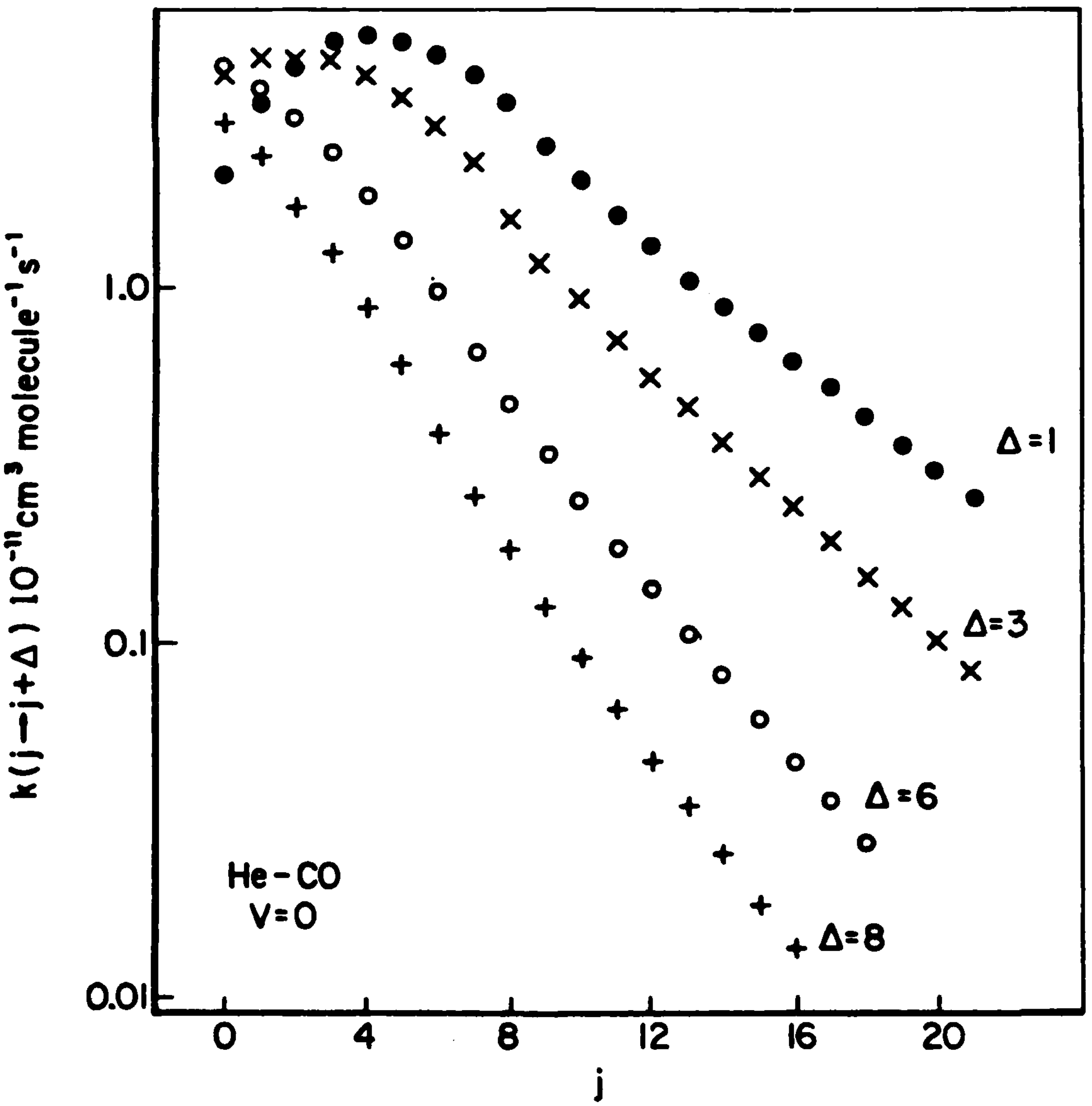

Figure 6. Single and multi-quanta R-T excitation rate constants for CO in V = 0 colliding with He.

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: Comparison with a Quantum Scaling Expansion", J. Mol. Spec. submitted (1982).
2. J. BelBruno, J. Gelfand and H. Rabitz, "Collision Dynamical Information from Pressure Broadening: Application to Carbon Monoxide", J. Chem. Phys. submitted (1982).
3. J. BelBruno, J. Gelfand, W. Radigan and K. Verges, "Helium and Self Broadening in the First and Second Overtone Bands of $^{12}C^{16}O$", J. Mol. Spec. in press (1 August 1982).
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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 Associated With This Contract

Mr. Keith Verges, Ph.D. Candidate
Ms. Elizabeth Wilczek, M.S., 1982
Dr. J. BelBruno, Postdoctoral Research Associate

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