V. ATOMIC RESONANCE AND SCATTERING

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1. STUDIES OF ROTATIONAL ENERGY TRANSFER

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The most probable type of inelastic collision involving molecules is Rotational Energy Transfer (RET), an important process in high-power gas lasers and interstellar clouds. We have measured rate constants for the RET process

$$Na_2^*(j_o) + X \rightarrow Na_2^*(j_o+\Delta) + X - \Delta E_r, \qquad (1)$$

where the * indicates that the Na_2 is in an electronically excited state, X is the target atom, j_o is the initial rotational quantum number, Δ is the change in rotational quantum number, and ΔE_r is the increase in rotational energy.

Since at typical temperatures roughly 100 rotational levels are populated, there are thousands of rate constants, $k(j_o \rightarrow j_o+\Delta)$, needed to characterize the system. Use

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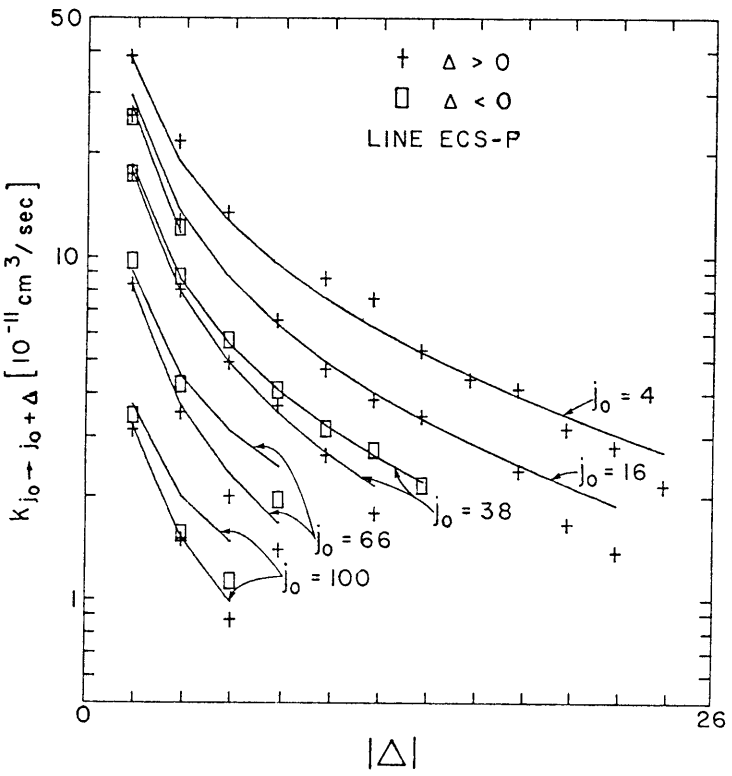

Fig. V-1. Measured Na_2^*-Xe rate constants, $k(j_0 \to j_0+\Delta)$, versus $|\Delta|$ for j_0 = 4, 16, 38, 66, 100. The lines connect points generated by the ECS-P fit.

of a computerized data-acquisition system and data-analysis programs have made possible accurate measurements of typically 50 to 100 level-to-level RET rate constants with j_0 ranging from 4 to 100 and $|\Delta| < 28$ for each of eight target gases: X = He, Ne, Ar, Kr, Xe, H_2, N_2, and CH_4. Figure V-1 illustrates the (apparently) complex dependence of the rate constants on j_0, $|\Delta|$, and the sign of Δ.

This unprecedented wealth of accurate data has made it possible for us to search systematically for fitting laws[1] — laws which express the hundreds of rate constants in terms of a few physically significant parameters. We have found a highly successful fitting law which combines the theoretically predicted Energy Corrected Sudden (ECS) scaling law with our empirically discovered[2] Power (P) law. The resulting fitting law, ECS-P, can fit 100 experimental rate constants with only 3 variable

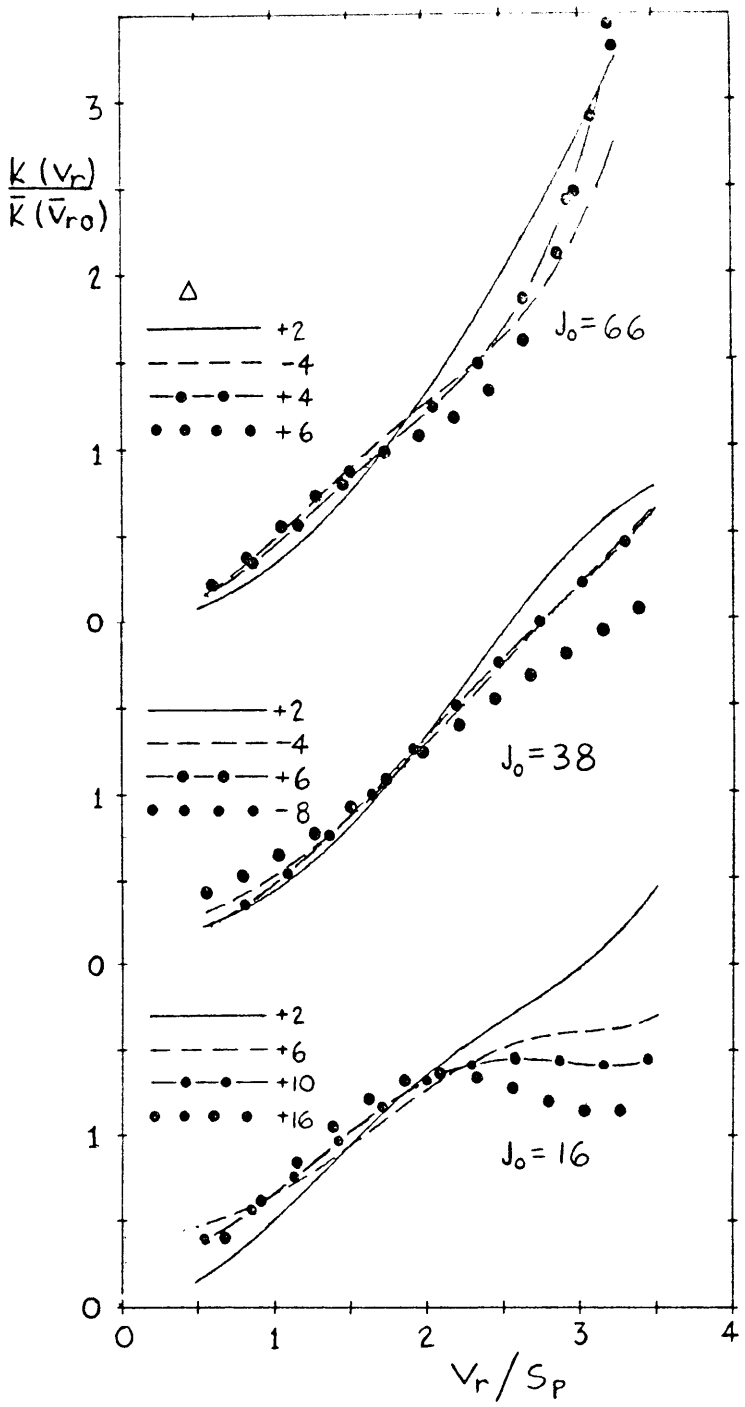

Fig. V-2. The normalized rate constants plotted versus the relative velocity v_r in units of a thermal velocity s_p.

parameters[3] to within our experimental error of ≃10%. In Fig. V-1 the ECS-P fit to the data, represented by the solid lines, reproduces the "complex" dependence of the rate constants on j_o and Δ. A comprehensive set of fits to various fitting laws of both our measurements and other accurate data has demonstrated the wide applicability of ECS-P.[4]

We have recently demonstrated[5] a new technique to measure the velocity dependence of the rate constants of process (1) which takes advantage of the Doppler effect. By simply tuning the laser, we can vary the mean-square collisional velocity (temperature) by more than an order of magnitude because when the laser is exactly tuned to line center it excites slow molecules, but when it is tuned slightly off-resonance, then only fast molecules are Doppler-shifted into resonance.

The results of our measurements for Na_2^* colliding with Xe are shown in Fig. V-2 where the normalized rate constant is plotted versus the relative velocity v_r in units of a thermal velocity s_p. The $j_o = 38$ data rise rather linearly with increasing velocity, indicating that the cross sections are fairly independent of velocity. For $j_o = 66$ the rates rise faster than linearly so the cross sections are rising with increasing velocity. These results seem to confirm the naive notion that the faster the molecules collide the more RET will take place. Surprisingly, the $j_o = 16$ rates actually fall off with increasing velocity, more so for the larger changes in angular momentum Δ. A possible explanation for this surprising behavior is that the long-range attractive intermolecular potential can suck slow-moving atoms in to undergo "hard" collisions more easily than fast atoms.

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2. LEVEL-TO-LEVEL ENERGY-TRANSFER DIFFERENTIAL CROSS SECTIONS USING DOPPLER VELOCITY ANALYSIS

National Science Foundation (Grant CHE79-02967)

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We have recently measured differential cross sections for rotational level-changing collisions in ground-state Na_2 with Ar[1]:

$$Na_2\ (v''=0,\ j_i=7) + Ar \rightarrow Na_2\ (v''=0,\ j_f) + Ar.$$

Measurements range in $\Delta j(j_f-j_i)$ from -4 to 80 and in θ from 0 to π.

The experiment is performed in a new differentially pumped crossed-beams apparatus capable of producing intense molecular beams with narrow velocity spreads ($\sim$10% FWHM) and internal temperature (typically 50°K). The Ar and Na_2 intersect at 90°. Two cw dye lasers make the level-to-level measurements: one laser (called the pump) modulates by optical-pumping the initial level population ($v''=0$, j_i); the other laser (called the analysis) measures the angular distribution of the final level ($v''=0$, j_f) using the ADDS method in which the angle of scattering is inferred from the Doppler shift.[2,3] Level-to-level scattering signals are isolated by phase-detecting the fluorescence from ($v''=0$, j_f) at the pump-modulation frequency.

Level-to-level cross sections, $\sigma_{i\rightarrow j}(\theta)$, are shown in Fig.V-3. All cross sections display a steep rise from zero to a maximum with a gradual decrease at larger angles. This maximum follows the empirical relation $1.4\ \Delta j + 20$. The scattering is dominated by the repulsive core of the intermolecular Na_2-Ar potential. Our observations can be qualitatively understood classically as follows: For a given molecular orientation and impact parameter there is an associated Δj and θ. When the impact parameter is small, the repulsive force is large, producing a large deflection θ and large integrated torque (i.e., Δj). As the impact parameter increases, the force decreases and so must θ and Δj. The maximum in $\sigma(\theta)$ for a particular Δj arises because there is, for a particular Δj, a minimum deflection angle with respect to orientation, and all orientations near this one give roughly the same deflection,

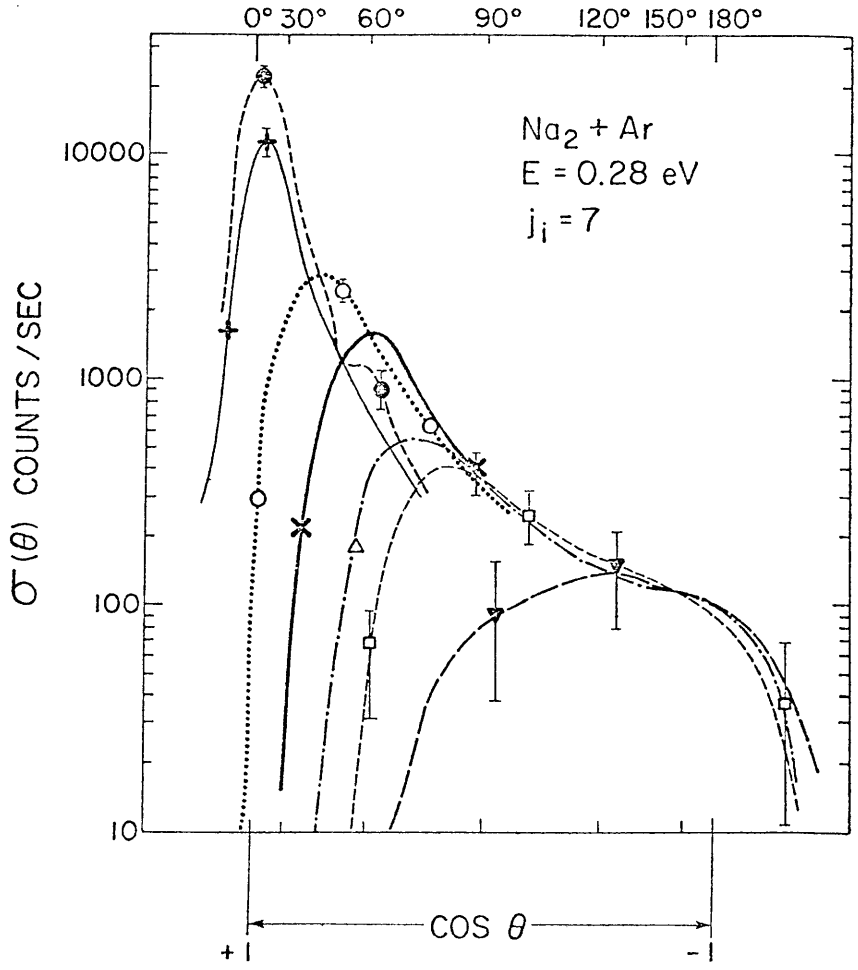

Fig. V-3. The level-to-level cross sections $\sigma_{j\to f}(\theta)$ for $j_i = 7$ are given in counts/sec vs θ (upper x-axis) and vs frequency offset or cos θ (lower x-axis). Each $\sigma(\theta)$ from 0 to π consists of approximately 40 data points; typical points with their error bars are shown. The existence of signal outside the nominal $0 < \theta < \pi$ range is due to imperfect resolution.

Legend: • $\Delta j = 2$; + $\Delta j = -4$; o $\Delta j = 16$; x $\Delta j = 28$; △ $\Delta j = 40$; □ $\Delta j = 48$; ▼ $\Delta j = 80$.

causing the maximum. We call this phenomenon a "halo" in analogy to the atmospheric optical phenomenon.

We plan to extend the present measurements to more initial levels and to different collision energies. Trends in the data will provide insight into the collision process, and the data itself should provide a sound basis for tests on different potential surfaces and current approximation methods used for calculating inelastic differential cross sections. The same experimental method can be extended to vibrational-energy transfer. Preliminary measurements will soon be under way.

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3. MOLECULAR SPECTROSCOPY

National Science Foundation (Grant PHY79-09743)

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The van der Waals group has been involved in laser spectroscopic studies of alkali-rare gas diatomics formed in a supersonic molecular beam. These weakly bound molecules ($D_{eX} \sim 1$ meV) are interesting theoretically and experimentally. Special conditions are necessary to produce the molecules (supersonic beam), and the potential energy surfaces extracted from the data serve as a check for theoretical calculations[1] and provide insight into interpretation of line broadening[2] and scattering experiments.[3]

Earlier work[4] done on NaNe has been expanded to include analysis of the $B^2\Sigma^+$ state. A more definitive vibrational assignment of the $A^2\Pi_r$ - $X^2\Sigma^+$ manifold has been developed using long-range theories.[5,6] A deperturbation analysis which

involves fitting the data to a model Hamiltonian and calculating RKR potentials, and then deducing Franck Condon factors is in progress.[7]

Laser excitation of NaAr formed in a beam has yielded $A^2\Pi_r$ - $X^2\Sigma^+(v,o)$ for 10 < v < dissociation, and several $B^2\Sigma^+$ - $X^2\Sigma^+$ bands. Analysis and application of long-range theories corroborates work done elsewhere[8] and provides new information on both the $A^2\Pi_r$ and $B^2\Sigma^+$ states.

Currently, using two photons of different energy, we are searching for a Rydberg state in NaAr which correlates to $Na(5^2S)$ + $Ne(^1S)$ in the separated atom limit. These states have potentials of theoretical interest but have never been observed before.

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