Simple Scaling Law for Rotational-Energy Transfer in Na_2*-Xe Collisions

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We have measured the thermally averaged rate constants for rotationally inelastic collisions of Na_2* and Xe for six values of initial angular momentum j_0 and for changes in j up to 30. We propose a new scaling law which fits all these rates within 20%. This scaling law implies that m_j is conserved in the collision, and shows that the square of the T matrix has a power-law dependence on the energy transferred. These results suggest the importance of dynamical effects in rotationally inelastic collisions.

In this Letter, we present measurements of rate constants for the rotational-energy–transfer (RET) process

$$Na_2^*(v_0, j_0) + Xe \rightarrow Na_2^*(v_0, j_f = j_0 + \Delta) + Xe - \Delta E_r, \quad (1)$$

in which the energy $\Delta E_r(v_0, j_0, j_f)$ is added to the rotational energy of the Na_2* in its $A^1\Sigma_u$ electronic state. RET is the simplest and most pervasive inelastic collision process between an atom and a diatom, and has been extensively studied both experimentally[1-8] and theoretically.[9-12] The dominant interpretive framework for this previous work is based on the general equation for the rate constant from level 0 to level f

$$k_{0f} = (2\pi/\hbar)\mathcal{T}_{0f}^2 \rho_T(E_f) N(j_0, j_f), \quad (2)$$

where $\mathcal{T}_{0f}^2$ is the integral over the scattering angle of the square of the average allowed transition matrix element from a state of level 0 to a state of level f, N is the angular momentum degeneracy factor which results from the average over initial magnetic quantum numbers, m_0, and the sum over m_f, and ρ_T is the density of translational states. (Interpreting experimental data requires that $\mathcal{T}_{0f}^2$ and ρ_T be averaged over experimental conditions.) The most widely used approach is to consider the logarithm of $\mathcal{T}^2$ (which is called the "surprisal") obtained when a particular value—called the "prior"—is assumed for N. The prior

$$N_\Delta = 2j_f + 1 \quad (3)$$

which is consistent with the statistical hypothesis (equal population in all degenerate states) is almost universally employed. It may be shown generally using information theory[13] and in some cases using quantum mechanics[14] that $\mathcal{T}^2$ should decrease as $\exp(-\theta|\Delta E_r|)$. This behavior is known as the exponential gap law and numerous workers have extracted values of θ from their RET data.[15,16]

The principal significance of our measurements lies in the fact that they conform to neither the statistical prior, N_Δ, nor the exponential gap law; rather they suggest a new scaling law for RET. For the data presented here, this scaling law uses the prior

$$N_0 = (2j_< + 1)/(2j_0 + 1), \quad (4)$$

where $j_<$ is the smaller of j_0 and j_f. In addition, T^2 varies as a *power* of the energy gap, i.e., as $|\Delta E_r|^{-\gamma}$. In this Letter we describe our experiment and present the results. We show that the prior N_0 results from a restriction on the change of magnetic quantum numbers $\Delta m_j = m_f - m_0$. Finally we emphasize that the existence of selection rules for Δm_j plus the power-law dependence (with $\gamma = 1.0$ within experimental error) strongly suggests the predominance of dynamical over the statistical considerations which underlie the N_Δ prior and the exponential gap law.

Our apparatus contains the three basic elements common to other energy-transfer experiments of this type[1-4]: a heated oven containing Na_2 (and Na) vapor plus a controllable amount of Xe target gas, a laser-light source which shines light through windows along one axis of the oven, and a monochromator which spectrally analyzes the fluorescence which exits a window in a perpendicular direction. Our experiment consists of setting a Coherent Model 599 cw dye laser to excite the desired v_0, j_0 molecular level and recording the fluorescence spectrum at several Xe pressures. The v_0, j_0 assignment is made by analysis of the P-R doublets in the fluorescence using standard techniques[17] in conjunction with the Dunham coefficients for Na_2.[18] Data in each scan are corrected for instrumental effects such as counter dead time and background and then each line in the spectrum is fitted to extract its height

and position. The relative population of each v_0, j molecular level is then determined by adding together the intensities of a pair of P and R lines which originate from it. (The radiative lifetime[19] does not depend on j.)

To determine the rate constant from the level populations we had to correct for multiple collisions and for the effects of vibrationally inelastic collisions. Our correction for multiple collisions was based on an exact solution of the appropriate steady-state rate equations[1,7] using the assumption that the rate of collisional transfer from (v_0, j) to $(v_0, j+\Delta)$ depends only on Δ (for all rotationally inelastic collisions pertinent to the analysis of data taken at a given j_0 and Xe pressure). The dependence of the resulting collisional rates on Xe density is not linear because vibrationally inelastic collisions effectively reduce the lifetime of the excited Na_2*. The cross section for this process was found to be 120 Å^2 independent of j_0, and was held constant when fitting the Xe density dependence of the collisional rate to find the rate constant for each value of Δ. All rate constants reported here were determined for Xe densities below 2×10^{16}/cm^3 where corrections for multiple and vibrationally inelastic collisions were at most 10% and 12%, respectively. The radiative decay rate exceeded twice the sum of all collision rates.

Results for $j_0 = 16$ and 54 are shown in Fig. 1; the requirement that Δ be even results from symmetry considerations.[20] The dramatic decrease of k at fixed $|\Delta|$ for larger j_0 suggests that the rate decreases more in response to rotational-

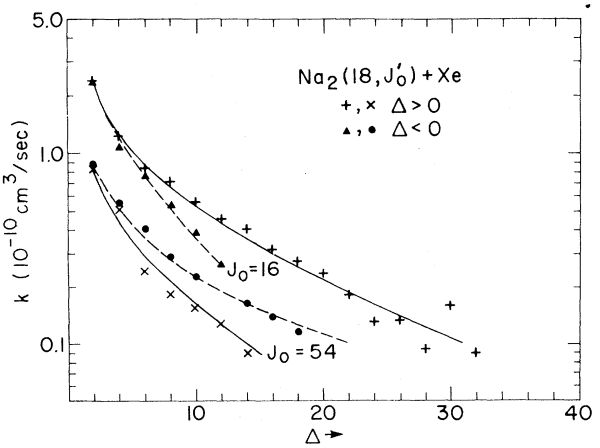

FIG. 1. Plot of measured rate constants vs Δ. The solid lines are fitted to the $|\Delta| > 0$ points and the dashed lines are fitted to the $\Delta < 0$ points; both fits used Eq. (5).

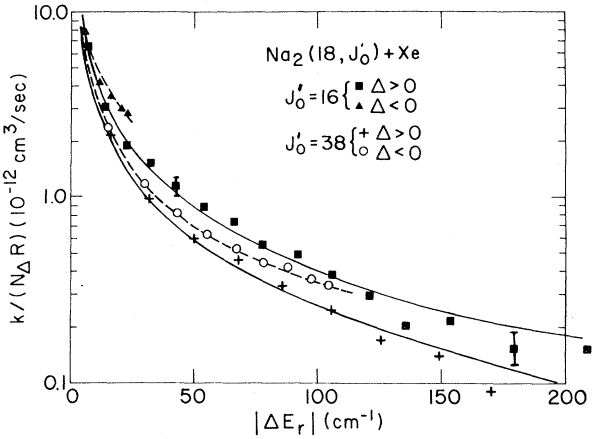

FIG. 2. Plot of $k/N_\Delta R$ vs $|\Delta E_r|$. This is equivalent to a surprisal plot assuming the most common prior rate and would be a straight line if the exponential gap law held. Solid lines are fits for $\Delta > 0$ points and dashed lines for $\Delta < 0$ using power law [Eq. (5)].

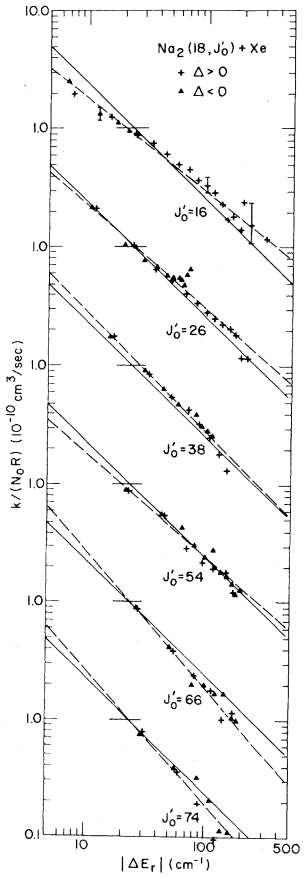

FIG. 3. Plots of k/N_0R vs $|\Delta E_r|$. The solid line in each plot is a power law using the average fit coefficients. The dashed lines are power-law fits to data from each j_0 separately. The top plot shows three representative error bars.

TABLE I. Power-law–fit coefficients.

j_0	16	26	38	54	66	74	All
a	0.48(3)	0.53(4)	0.54(5)	0.44(6)	0.41(6)	0.43(8)	0.47
γ	0.80(10)	0.89(12)	1.02(12)	0.87(15)	1.18(16)	1.12(18)	0.98

energy transfer ΔE_r than to Δ, and indicates that models of RET in which angular-momentum transfer predominates[21,22] may not conform well to the data.

Figures 2 and 3 show a presentation of the $\mathcal{T}^2$ matrix deduced from our data using the priors N_Δ and N_0, respectively. The quantity $R(\Delta E_r, T)$ is the ratio of $\rho_T(E_f, T)$ and $\rho_T(E_0, T)$ at temperature T. The prior N_0 is preferable to N_Δ for two reasons: It removes the conspicuous asymmetry of the data with respect to the sign of Δ, and it removes the systematic dependence of $\mathcal{T}^2$ on j_0. The preference for the prior N_0 can be explained as originating from conservation of m_j.

It is clear from Fig. 3 (log-log plot) that $\mathcal{T}^2$ has an inverse power dependence on ΔE_r. Since the replacement of N_Δ by N_0 changes the shape of $\mathcal{T}^2$ not at all for $\Delta < 0$ and only slightly for $\Delta > 0$, it is clear that a power law would also fit $\mathcal{T}^2$ if N_Δ were employed. Table I shows the values of a and γ for fits to k of the form

$$k(j_0 \to j_f) = a \left| \frac{\Delta E_r}{50\ \mathrm{cm}^{-1}} \right|^{-\gamma} R(\Delta E_r, T) N_0(j_0, j_f). \quad (5)$$

Except for a small systematic decrease of γ for $j_0 = 16$ (and possibly 26) there is no systematic variation of a or γ with j_0. A single power-law function using the average value of a and γ (called "all" in Table I) represents all the data we have presented surprisingly well, and inclusion of a factor proportional to $\exp(-b|\Delta E_r|)$ does not significantly improve the χ^2 for the fit. Additional data with ~10–15% statistics taken from $(v_0, j_0) = (13, 26)$ and $(28, 36)$ yield the same γ values as the data with $v_0 = 18$, but the value of a is significantly lower for $v_0 = 28$. We cannot offer a physical explanation for the power-law behavior.

The physical basis of the prior N_0 is the conservation of m_j: If $\Delta m_j = 0$, then there will be only $2j_< + 1$ open channels in the sum over m_0 and m_f, and the factor $(2j_0 + 1)^{-1}$ will arise from the average over m_0. The prior N_Δ, in contrast, results when there is no selection rule on Δm_j. Several recent theoretical approximations applicable to RET involve an m-conserving assumption, including the j_z-conserving approximation[23] and the p-helicity-decoupling approximation[24] in which m is conserved relative to the atom-diatom axis and relative to the direction of the linear momentum, respectively. Experimental evidence from the polarization of rotational satellites[25] in I_2 collisions suggests that m_j is conserved in a space-fixed coordinate system. Because the present experiment measures quantities which have been averaged or summed over m_0 and m_f it is not capable of discriminating among these different m-conserving models. On the other hand, our experiment shows that m conservation has a dramatic effect on the angular-momentum statistics of the orientation-averaged rates. We suggest that other measurements and experiments be examined for similar evidence of m conservation.[23]

The striking power-law dependence of $\mathcal{T}^2$ on ΔE_r observed here for Na_2*-Xe appears to have a wide applicability in other studies of RET. Preliminary investigation of calculated RET rates in H_2-Li^+, CO_2-Ar, and N_2-Ar,[16,26,27] and experimental rates for $LiH(j_0 = 1) + Ar$,[28] reveals that a power law represents *all* of these data better (χ^2 are reduced by factors ranging from 1.5 to 25) than an exponential gap law, and that γ ranges between 0.8 and 1.2. We feel that these observations, together with the observation of the m_j-conserving selection rule, should serve as a strong stimulus for the development of dynamical theories of RET.

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Charge-State Dependence of Molecular-K-X-Ray Production in Nearly Symmetrical Ion-Atom Collisions

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We have observed for the first time a pronounced increase of the molecular-K-x-ray production as a function of projectile charge state in 32-MeV S+Ar (gas target) collisions. The results are interpreted as evidence for strong excitation of $1s\sigma$ electrons into empty high-lying bound states. A comparison of this gas-target system and the solid-target systems Cl+Cl establishes unambiguously the predominance of one-collision processes for molecular-K-x-ray production.

The direct formation of vacancies in the $1s\sigma$ quasimolecular state in symmetric heavy-ion collisions plays a fundamental role in the production of molecular K x rays[1] and in the possible observation of spontaneous positron emission in overcritical fields.[2] It also accounts for the K-vacancy production cross section of the higher collision partner in sufficiently asymmetric collisions where the $2p\sigma$-$1s\sigma$ vacancy-sharing process is negligible.[3] So far, most approaches have only considered the excitation of $1s\sigma$ electrons into the continuum, i.e., ionization.[4] In a recent calculation[5] Betz *et al.* have shown that excitation of $1s\sigma$ electrons into high-lying bound states (if a vacancy is present) can be considerably larger th than the excitation into the continuum. In this Letter we present first measurements of the projectile charge-state dependence of the absolute cross section of molecular K x rays emitted in S+Ar (gas target) collisions which provide experimental