Doppler-Resolved Kinetics of Saturation Recovery

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ABSTRACT

Frequency modulated laser transient absorption has been used to monitor the ground state rotational energy transfer rates of CN radicals in a double-resonance, depletion recovery experiment. When a pulsed laser is used to burn a hole in the equilibrium ground state population of one rotational state without velocity selection, the population recovery rate is found to depend strongly on the Doppler detuning of a narrow-band probe laser. Similar effects should be apparent for any relaxation rate process that competes effectively with velocity randomization. Alternative methods of extracting thermal rate constants in the presence of these non-thermal conditions are evaluated. Total recovery rate constants, analogous to total removal rate constants in an experiment preparing a single initial rotational level, are in good agreement with quantum scattering calculations, but are slower than previously reported experiments and show qualitatively different rotational state dependence between Ar and He collision partners. Quasi-classical trajectory studies confirm that the differing rotational state dependence is primarily a kinematic effect.

1. Introduction

The use of high resolution lasers to monitor the time evolution of rovibrational state distributions and their velocity distributions is common practice. Non-equilibrium velocity distributions can be monitored with sub-Doppler frequency resolution, for example, in photofragmentation,^{1,2,3} hot atom thermalization,^{4,5} or photoinitiated bimolecular collision products.^{6,7} The use of a Doppler shift for velocity selection to study velocity-dependent reaction cross sections has been applied to rotational energy transfer (RET) in excited states,^{8,9} and in

Doppler-resolved double-resonance methods,^{10,11,12} where corrections for Doppler selection are commonly applied in careful kinetic studies of energy transfer.^{11,13,14} The competition among optical excitation, velocity-changing collisions, and inelastic collisions plays a central role in a substantial body of classic work on collisional effects in sub-Doppler saturation spectroscopy and speed-dependent collisional broadening.^{8,15,16,17,18,19} Observations similar to those in the present report have been noted in the context of inelastic and depolarizing collisions of the A state of CN in the laboratory of Costen and McKendrick.^{20,21}

For chemical kinetics measurements, velocity-specific detection can be an inconveniently specific tool, in the same way that rotationally resolved spectroscopic rate measurements can be complicated by changing non-thermal rovibrational distributions for reactions that compete with rotational thermalization.²² For relatively slow reactions performed at high enough pressures, fast rotational energy transfer can maintain thermal rotational distributions, and similar rates are observed for any rotational state. Similarly, if velocity randomization collisions compete effectively with those reactive or energy transfer processes that discriminate among velocities, the Doppler line shape will remain thermal, at the local temperature of the bath gas. Under these conditions, only the signal amplitude and not the kinetics will vary with Doppler detuning.

In contrast, our recent experiments to measure rotationally inelastic rates for ground state CN radicals by saturation recovery kinetics revealed a large, systematic variation in the signal recovery rates as a function of the Doppler detuning. The observations may seem at first surprising, since, unlike the earlier reports of initial Doppler selection and subsequent translational thermalization,⁸⁻¹⁴ the transient bleaching of our probed rotational states is performed without Doppler selection, yet the Doppler spectrum of the depletion, or “hole,” shows rapid translational cooling in the initial stages of the return to equilibrium. This report

characterizes the Doppler-resolved kinetics measured under these conditions, and the inelastic and elastic collisions that account for these effects.

Following a description of the experimental details of the double-resonance kinetic measurements in section 2, we describe the qualitative features of the saturation recovery experiment in section 3.1. An analysis based on a time-sequence of spectra is presented in section 3.2, and an alternate global analysis formulated in terms of speed-dependent rates is presented in section 3.3. Consistent thermal rate constants for total recovery due to rotational energy transfer through collisions with either He or Ar, and the photolytic precursor CH_3COCN are obtained using either method. Section 4.1 includes a comparison of the present RET rates with previously published experimental and theoretical values. New quantum inelastic scattering calculations for $\text{Ar} + \text{CN} (X^2\Sigma^+)$ were carried out as part of this work. The qualitatively different rotational-state dependence of RET total removal rate constants with He and Ar is discussed in section 4.2 with the help of some quasi-classical trajectory calculations. The connections between the present measurements and speed-dependent relaxation and velocity changing collisions are briefly discussed in section 4.3. An analysis of depolarization kinetics and saturation transfer kinetics, and a more thorough comparison with theory are reserved for a subsequent report.

2. Experimental Methods

Elastic and inelastic collisions of the CN radical $X^2\Sigma^+, v = 0$ ground state were studied using a V-type optical-optical double resonance scheme to monitor the kinetics of ground state saturation recovery. Many features of the experiment have been described in our previous reports of sub-Doppler saturation spectroscopy^{23,24} and pressure broadening studies of the CN A-X transitions,²⁵ using a frequency modulated, continuous wave Ti:sapphire laser to probe the CN radical. In this

work, saturation was performed with a ns pulsed dye laser to deplete a chosen ground state level without Doppler selection. The experimental setup is shown in Figure 1. CN radicals were produced by 193 nm excimer laser photolysis of pyruvotrile, CH_3COCN , (Aldrich, >90% purity) in a 65 cm flow cell fitted with wedged, fused silica windows. The frequency-modulated (FM) probe laser was used to monitor CN radicals on selected rotational transitions near 900 nm in the CN $A^2\Pi \leftarrow X^2\Sigma^+$ ($v = 1 \leftarrow 0$) band. The radio-frequency power into the modulator was adjusted to give a modulation index $M = 0.55$, corresponding to first-order sidebands each with about 8% of the residual carrier frequency power, as determined with an optical spectrum analyzer. The probe beam was collimated to a beam diameter of 1-2 mm, entirely contained within the much larger photolysis volume, produced by ~ 5 mJ in a 1 cm^2 pulse at 193 nm. The bleach beam came from a YAG-pumped dye laser tuned between 620 and 625 nm to saturate selected rotational lines in the CN $A^2\Pi \leftarrow X^2\Sigma^+$ ($v = 4 \leftarrow 0$) band. The bleach beam pulse energy was typically adjusted to 1-1.5 mJ/pulse with polarization optics and then passed through a fused silica photoelastic modulator, synchronized with the YAG Q-switch timing to allow software control of its polarization during the scan.

The counterpropagating bleach and probe beams crossed at an angle of 0.5° , with the probed volume mostly contained within the larger bleached volume. Premixed samples of pyruvotrile and He or Ar were prepared at dilutions between 1:10 and 1:100 and introduced to the sample cell through a mass flow controller. The inlet flow rate was maintained at 5 sccm and the total steady-state pressure was adjusted with a throttled and liquid-nitrogen-trapped mechanical pump to give 10 mTorr partial pressure of the photolytic precursor at total pressures between 100 and 1000 mTorr, as monitored with a capacitance manometer.

The optical receiver consisted of a fast Si photodiode (Hamamatsu S3883) viewing the probe beam transmitted through the sample cell. The amplified RF component of the photodiode signal was demodulated in an I&Q demodulator, referenced to the local oscillator at 192 MHz. The in-phase (I) and quadrature (Q) components were low-pass filtered (Minicircuits SBLP-39) and averaged on a digital oscilloscope to give 4000-point transient waveforms spanning 20 μ s. Typical scans used 100 excimer shot averaging for three cycles at each wavelength step of the probe laser: one with the bleach beam polarized parallel to the probe beam polarization, one with the bleach beam blocked with a shutter and a third with the bleach beam perpendicular to the probe beam polarization. A pair (I&Q) of transient waveforms was archived for each of these three cases at 50-60 probe frequency steps of $\sim$ 80 MHz across the Doppler profile, along with wavemeter data, for subsequent analysis.

3. Results

3.1. Photolysis, Saturation and Recovery. A typical raw saturation recovery signal at a probe frequency near the peak FM signal for a CN transition is shown in Figure 2. The demodulated and low-pass filtered transient waveform is plotted against time, with the excimer photolysis laser firing $\sim$ 12 μ s prior to the time origin, when the bleach laser fires. For this example, the probe laser is tuned to a maximum of the FM signal of the $P_2(6)$ line of the (1-0) band, while the bleach laser is tuned to the center of the corresponding $P_2(6)$ line of the (4-0) band. It can be seen that the initial signal at the time of photolysis is small and grows for several μ s, while both the rotational and translational distributions cool from hot nascent values, as investigated earlier.²⁶ Fitting the time-delayed FM Doppler spectra shows effective translational temperatures decreasing from above 1300 K at early times down to about 300-320 K at the time

of the bleach laser pulse. The initial rotational distribution of CN in $v = 0$ can be characterized by a temperature near 1800 K,²⁶ but at the pressures used in these experiments, it too becomes nearly stationary, near room temperature after 5-10 μ s. The thermal CN signal persists for over 100 μ s, but is lost through slow reactions, diffusion and pump-out long before the next excimer pulse 100 ms later.

The inset to Figure 2 expands the time scale around the time of the bleach laser, and displays the fractional depletion signal at this probe frequency as a function of time for one polarization geometry. The depletion amplitude is obtained by subtracting the unbleached reference waveform from the bleached transient waveform. To correct for any variation in the excimer power or sample concentration between the reference and the bleached cycles at each step of the frequency scan, the reference waveform is scaled by the ratio of bleached to unbleached signals in a time gate immediately prior to the arrival of the bleach laser pulse, a scale factor typically between 0.98 and 1.02. Each scan is initially processed to give a time-dependent depletion amplitude for I and Q channels in each of the two polarization geometries, yielding FM depletion signal vs. time and frequency, for subsequent analysis described below. Division of the depletion amplitude by the slowly decaying unbleached reference signal yields the fractional depletion, which represents pure rotational redistribution of a normalized population, as illustrated in Figure 2.

The recovery kinetics are a measure of the redistribution of population among the rotational states of CN ($X^2\Sigma^+$, $v = 0$) following a partial, permanent removal of the population of one rotational state due to the bleach laser. On the ns time scale of bleaching, the selected rotational level of the ground state is depleted to a fraction of its initial Boltzmann equilibrium population, while creating an excited state population in $v = 4$ of the A state equal to lost population of the

ground state. The A state radiative lifetime in $\nu = 4$ is about $4 \mu\text{s}$ ²⁷ with a Franck-Condon factor that limits the repopulation of $\nu = 0$ in the X state to only about 1% of the radiative relaxation from $\nu = 4$ in the A state,²⁸ and the vibrational relaxation in the X state is also negligibly slow on the time scale of rotational energy transfer. Quenching by rare gas or the pyruvitrile precursor will reversibly populate isoenergetic high vibrational levels of the X state,^{27,29,30} which are metastable on the μs time scale of the rotational energy transfer measurements. Consequently, the excited molecules are effectively removed irreversibly from the $\nu = 0$ in the X state, and the subsequent relaxation kinetics depends only on the rotational redistribution within this vibrational level and the much slower reactive and diffusive loss of the total ground state population.

The kinetics of depletion recovery, following the partial bleaching of a single rotational state from a thermalized distribution is isomorphic to the kinetics of relaxation of the same state, initially prepared in an otherwise empty rotational manifold.³¹ The kinetic master equation is the same and the initial conditions differ only by a sign change in the perturbation, and the addition of the stationary eigenvector (the Boltzmann rotational distribution). With appropriate normalization, the kinetics are identical and the same information can be extracted from either type of experiment.

The linearly polarized bleach laser creates an aligned excited state population, leaving behind a ground state hole with the complementary alignment. The probe signal thus depends on the relative polarization of bleach and probe lasers. The transient depletion recovery amplitudes for parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) polarizations can be written as

$$\begin{aligned} I_{\parallel}(t, \omega) &= C g_D(\omega, t) A_0^0(t) \left(1 + h^{(2)} A_0^2(t)\right) \\ I_{\perp}(t, \omega) &= C g_D(\omega, t) A_0^0(t) \left(1 - \frac{1}{2} h^{(2)} A_0^2(t)\right) \end{aligned} \quad (1)$$

where C is a constant including laser powers, optical path length, linestrength and instrumental factors; $h^{(2)}$ is the rank 2 depolarization factor^{32,33} for one-photon absorption, and $g_D(\omega, t)$ is a normalized Doppler lineshape function, generally time-dependent, but in this case negligibly dependent on the polarization. The alignment can be cancelled with the weighted sum $(I_{\parallel} + 2I_{\perp})$ to yield a time-dependent signal proportional to the isotropic population depletion, $A_0^0(t)$. The polarization difference, $(I_{\parallel} - I_{\perp})$, when normalized to the isotropic depletion, is proportional to the alignment moment of the hole, $A_0^2(t)$. We devote the present report to the analysis of the isotropic population change, $A_0^0(t)$, and defer treatment of the depolarization kinetics to a subsequent report.

3.2 Spectral evolution of the CN hole. The time-dependent spectrum of the isotropic depletion is initially thermal, with the same translational temperature as the CN population prior to saturation. Including power broadening, the effective line width of the multimode dye laser used for bleaching is large enough to saturate the transitions without detectable velocity selection. Successive time slices of the I and Q channel FM depletion amplitudes were fit to thermal lineshape functions, with an adjustable temperature, Doppler-integrated intensity (proportional to the total depletion), and a phase angle representing the complementary combinations of dispersion and absorption contributions to I and Q channel signals. The absorption-phase FM spectra resemble Gaussian first derivative lineshapes, and the dispersion-phase FM spectra resemble second derivatives of the associated dispersion lineshapes, as described in further detail elsewhere.^{20,25,34,35} As an example of the time-dependent depletion spectra and the thermal fits, Figure 3 illustrates absorption- and dispersion- phase FM spectra in individual 5-ns time slices selected at 50, 150, and 250 ns following the bleach laser pulse. The

data shown are for probing and bleaching $R_1(0)$ rotational lines in a sample containing 590 mTorr of Ar and 10 mTorr of the precursor. I and Q channel FM depletion signals are polarization averaged and plotted as phase-rotated linear combinations using the optimized phase angle from the least squares fit. The best fit thermal absorption and dispersion lineshapes, shown as solid lines, share for each time slice a common temperature and a single adjustable amplitude, proportional to the Doppler-integrated depletion. Substantial translational cooling is observed on this timescale. The temperature of the hole drops ~ 35 K per 100 ns, which is the approximate $1/e$ time of the depletion recovery for this sample and rotational state. Some elementary remarks and further illustrations of the effects of narrow-band probing of relaxation kinetics when accompanied by translational cooling are presented in Supplement 1 of the Supplemental Information for this paper.

Figure 4 illustrates the time-dependent temperature and the corresponding total depletion recovery kinetics for a dense set of time slices from the same data set used in Figure 3. The Doppler-integrated total depletion amplitudes are shown as linear (4a) and logarithmic (4b) plots for this example scan where the translational cooling is very clear. The spacing of displayed data points becomes sparser at longer times, as we have averaged over increasingly larger time bins in order to control the uncertainties in the fits to the signals of decreasing amplitude. Pressure broadening of the $A-X$ CN transitions²⁵ at a maximum pressure of 1 Torr will contribute a Lorentzian broadening with less than 1% of the Doppler width, and is not included in the present analysis.

Figure 4a shows a rapid initial translational cooling followed by slow reheating back to the ambient temperature. The depletion recovery kinetics shown in Figure 4b and 4c are typical of many state-resolved energy transfer measurements^{13,36,37,38,39} where the initial decay is

exponential, at a rate indicative of the total removal (recovery) process, but then decelerates as multiple collision effects start to become significant, and finally a new thermalized signal level is attained, once the population (depletion) has been rotationally equilibrated. Master equation treatments can relate a full matrix of state-to-state RET rate constants to the full multi-collision time evolution from an arbitrary initial condition, but the initial log slope of the decay of a directly populated state's population (or depletion) can be shown to give directly the total removal (recovery) rate without approximation.³¹

A set of depletion recovery measurements was made for seven rotational states at a series of concentrations of pyruvitrile in He and in Ar, always adjusting the total pressure to maintain the partial pressure of pyruvitrile at 10 mTorr. Transitions chosen were $R_1(0)$, $P_2(4)$, $R_1(4)$, $P_2(6)$, $P_2(10)$, $R_1(13)$ and $Q_1(17)$, using the corresponding transitions in the 4-0 and 1-0 bands for bleach and probe processes. The rotational states were chosen to span a range of thermally populated levels that could be probed and bleached without interference from nearby or blended lines. One pair of lines, $P_2(4)$ and $R_1(4)$, was chosen to probe independently the F_1 and F_2 ($J = 5.5$ and 4.5) spin-rotation levels of the $N = 4$ rotational state, an example of a measurement that could not be done with $B-X$ spectroscopy, where the spin rotation doublets are unresolved at low N . No significant difference in the RET rates was observed between these two spin-rotation levels, as expected from the quantum scattering calculations.

A time series of thermal fits to the FM depletion signals, as depicted in Figures 3 and 4, was performed for each scan, and the time-dependent, Doppler-integrated, total depletion amplitudes were fit to a single exponential during the first 50% of the first time constant ($t < 1/2\tau$). The initial decay rates were corrected for the slow decay of the reference signal observed in the absence of the saturation pulse. The slope of the corrected initial decay rates with respect to the

He or Ar partial pressure produced the estimates of the total recovery rate constants listed in the third columns of Tables 1 and 2, with 1σ uncertainties derived from the scatter in the linear fits.

3.3 Speed-dependent relaxation rates. An alternate analysis method was developed that does not depend on independently adjusted temperature fits to each time slice, thereby avoiding the amplitude noise that is correlated with the poorly determined temperature at longer times as the intensity decreases. A global fit to each entire time and frequency-dependent FM depletion signal was implemented, based on an empirical functional form with only a few adjustable parameters, and an analytic means of extracting the initial decay rate, evaluated at the initial temperature.

The relaxation rate is expressed as an explicit function of the probe laser detuning, inspired by the increasing average relative collision velocity of thermal bath molecules with a Doppler-selected velocity group of probed molecules:

$$k(x_D) = k_0 \sqrt{1 + b x_D^2} \quad (2)$$

Here, x_D is the dimensionless Doppler shift

$$x_D = \frac{(\omega - \omega_0) c}{\omega_0 \sqrt{2k_B T / m}} \quad (3)$$

where $\omega - \omega_0$ is the detuning from line center in cm^{-1} , and m is the CN mass. The rate at line-center is k_0 , and b is a dimensionless adjustable parameter to characterize the speed-dependence of the relaxation rate in a bath of constant temperature T . The functional form of Eq. (2) is motivated by the rms collision velocity of a Doppler selected particle colliding with a thermal target molecule. If the total inelastic cross-section is independent of velocity, and velocity changing collisions do not compete with inelastic collisions, and the collisions of CN with the

undissociated precursor can be neglected, then the relaxation rate for the Doppler-selected velocity group would follow this form, with b determined entirely by the masses of the collision partners. Allowing b to float gives a single effective parameter to represent the speed dependence of the relaxation rate that subsumes all the ways these idealizations can be wrong. The adequacy of the representation will be assessed in section 4.3 below.

At each detuning x_D , the time-dependent relaxation signal is represented as

$$A(x_D, t) = \left(e^{-k(x_D)t} + A_\infty \right) G_0(x_D) e^{-k_{loss}t} \quad (4)$$

where $G_0(x_D) = \alpha e^{-x_D^2}$ is a time-independent thermal Gaussian lineshape function, including a single global amplitude, α , and characterizing the identical initial and final temperatures T through the implicit frequency scaling of x_D . The slow loss of total population during the rotational relaxation is included with the damping factor $e^{-k_{loss}t}$. The background loss rate, k_{loss} varied between 2×10^4 and $7 \times 10^4 \text{ s}^{-1}$, as determined independently from the unbleached transient data recorded in each scan. The functional form of single exponential decay to a final offset is exact for a two-state reversible system returning to equilibrium, as if the bath of all unobserved states were an undifferentiated kinetic species with a single reverse rate to the probed level, and often provides a good, though not exact representation of total RET kinetics.^{40,41} By restricting the temporal region of interest to the initial stages of relaxation, prior to attainment of full equilibrium, the functional form is flexible enough to represent accurately the type of decelerating decay illustrated in Figure 4c for times as long as 2 or 3 time constants. The adjustable parameter A_∞ can then be reinterpreted not as the true equilibrium Boltzmann population ratio of the detected state to the sum of all other states, but rather as an empirical deceleration parameter, representing the curvature of the initial log decay.

One advantage of this functional form is that it represents a larger and more accurately determined data set, and one can analytically evaluate the thermally averaged decay rate at $t = 0$ from the global fit parameters k_0, A_∞ and b .

$$k_{ave} = \frac{k_0 f(b)}{(1 + A_\infty)}, \quad (5)$$

where the thermal average over the speed-dependent rate gives a correction factor

$$f(b) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-x_D^2} \sqrt{1 + b x_D^2} dx_D. \quad (6)$$

Over the range of interest in the present experiments, with $0 < b < 1$, this function is well described by the quadratic approximation $f(b) \approx 1.000 + 0.2385 b - 0.0389 b^2$, which represents the factor by which the thermally averaged rate exceeds the rate for the cooler velocity group probed at line center.

A nonlinear least-squares fit was implemented in MATLAB, adjusting a single initial temperature, T , the parameters k_0, A_∞, b , the line center of the transition, ω_0 , the overall signal amplitude, α , and a single DC baseline offset constant, to model the frequency-dependent saturation recovery kinetics $A(x_D, t)$ according to Equation 4. The parameters were optimized to minimize the squared difference between the experimental FM depletion signal in time and frequency and the model FM signal derived from $A(x_D, t)$ using the relation between absorption phase FM signals $A_{FM}(x_D)$ and the Doppler absorption spectrum $A(x_D)$ at each time:

$$A_{FM}(x_D) = \{A(x_D + x_{RF}) - A(x_D - x_{RF})\}(1 - M^2/8) + \{A(x_D + 2x_{RF}) - A(x_D - 2x_{RF})\}M^2/8. \quad (7)$$

Here $x_{RF} = \frac{\omega_{RF} c}{\omega_0 \sqrt{2k_B T / m}}$ is the modulation frequency ω_{RF} expressed in the same normalized

units as the Doppler shift, x_D . With the modulation frequency at 192 MHz and a typical CN

transition near 900 nm at 300K, x_{RF} is near 0.4. For the modulation index, $M = 0.55$, used in the present measurements, the correction for second-order sidebands included in Eq. 7 is small, and the third-order correction (not included in Eq. 7) is negligible.^{35,42}

An example of the resulting fits is illustrated in Figure 5, showing observed and calculated FM transient signals at different detunings, sampled from the saturation recovery measurements on the $P_2(4)$ line in a sample containing Ar at total pressure of 200 mTorr. The entire FM signal at all frequencies and over the illustrated time window ($0 < t < 2/k_0$) was fit with the minimal set of parameters listed above. The data within 50 ns of the time origin is given no weight in the fit due to the finite bandwidth of the detection, and increased uncertainties associated with phase correction during and shortly after the rapid depletion. The larger deviations between observed and fit kinetics at early times in Figure 5 reflect this. The illustrated decay curves show average signals at detunings corresponding to the maximum of the FM signal and at larger detunings where the FM signal is about half as large. The solid lines represent cuts through the three-dimensional global fit at the corresponding Doppler shifts, normalized to unit initial depletion amplitudes. It may be seen in this case that the decay is about 45% faster at the larger Doppler shift illustrated, which corresponds to a parameter b of 0.56 for this rotational state and sample mixture (10 mTorr CH_3COCN and 290 mTorr Ar).

The length of the time record included in the kinetic analysis using Eq. 4 introduces a model-dependent variation into the estimated initial rates that exceeds the statistical errors. Excluding data at times beyond two decay time constants allows A_∞ to float above the actual asymptotic value and allows the initial slope and curvature of the logarithmic decay to be described with an accurate empirical function. Restricting the fits to times much less than one decay time constant is inappropriate, since then k_0 and A_∞ are too closely correlated to be independently determined.

At times of three or more time constants, the approach to final equilibrium is more nearly complete, and A_∞ will be a good approximation of the final value, but the single exponential k_0 is then inadequate to represent the multi-exponential decay, and the model fits are systematically too slow at early times. Our preferred analysis includes data selected from the first two time constants of decay.

The thermally averaged, initial recovery rates defined by Eq. 5 are plotted against the partial pressure of He or Ar in Figure 6 for a sample of three rotational states. The slopes give the thermal rate constants for total recovery (removal) for the corresponding rotational state and collision partner, while the intercepts give the contribution due to the precursor, CH_3COCN at a constant partial pressure of 10 mTorr. The lines included in Figure 6 are the result of fits that constrain the He and Ar lines for the same rotational state to share a common intercept. Note that the precursor makes a significant contribution to the RET, increasingly so at low rotational states. The rate vs. He pressure lines are nearly parallel for the three illustrated states, revealing differences almost entirely accounted for by the change in RET due to the precursor. In contrast, the corresponding lines for Ar show a significant change in slope among the three illustrated rotational states. The same analysis applied to the entire set of saturation recovery measurements leads to the thermally averaged initial recovery rates listed in the fourth column of Table 1 for Ar and Table 2 for He, and in the third column of Table 3 for CH_3COCN .

To confirm the large and strongly N -dependent CN RET rates for CH_3COCN , we performed several additional measurements with a range of CH_3COCN partial pressures between 2 and 10 mTorr and a constant Ar partial pressure of 100 mTorr. The slopes of k_{ave} vs. the CH_3COCN partial pressure for three rotational states investigated lead to the rates listed in column 4 of

Table 3, which confirm the trends given by the intercepts of the more extensive He and Ar-dependent measurements.

The values of the speed-dependent parameters b from the global fits are plotted for multiple rotational states as a function of He and Ar partial pressure in Figures S4 and S5 in the Supplemental Information. Error bars denote 1σ uncertainties derived from the least-squares fit, although the variation with pressure and among rotational states is more irregular than these statistical errors, suggesting additional systematic errors in the determination of the speed-dependent b parameters. Fortunately, the propagation of uncertainty in b to the thermally averaged rate constants is modest, with a 50% uncertainty in b resulting in only a 4% error in the corrected thermal rate constant for typical values of b around 0.3.

4. Discussion

4.1 Comparison of total RET rates with previous experiments and theory. The rate constants for total rotationally inelastic energy transfer measured in these studies differ from previously reported values by Fei et al. for both He³⁷ and Ar⁴³ collisions, as can be seen in Tables 1 and 2. Their experiments used stimulated emission pumping of selected rotational states of CN ($X^2\Sigma^+$, $v = 2$), and measured the disappearance of the pumped level and the appearance of population in unpopulated levels as a function of delay time by pulsed laser induced fluorescence. Our rate constants are slower by as much as a factor of 2 compared to the previously published values, and in particular, show a qualitative difference in the rotational state dependence. The decrease in rate constant for increasing rotational levels observed for Ar collisions is replaced for He collisions by a near independence of the RET rate on rotational states (at least up to $N=17$) in our measurements. What can cause these differences? Our measurements were performed with rotational states in $v = 0$ compared to the previous

measurements in $v = 2$, but no strong variation in RET among nearby vibrational states is expected.^{44,45} Our measurements resolve the F_1 and F_2 spin-rotation levels, so that our total recovery rates include an additional contribution from the nearly elastic spin-rotation state-changing collisions that are not part of the measurements with the unresolved spin-rotation doublets in the $B-X$ LIF measurements – not a reason for our measured rate constants to be *smaller* than those measured by LIF. Because of the very good agreement of the state-to-state RET rate constants reported between the previous SEP/LIF experiments³⁷ and the quantum scattering results of Lique et al.⁴⁵ and the reasonable expectation that the total removal rate constants should be decreasing at higher rotational levels due to exponential energy gap arguments, we searched hard for possible systematic problems with our method of FM spectroscopy in the depletion recovery mode for the determination of RET rate coefficients, and in particular, the quantitative consequences of the observed translational cooling on the extraction of rate coefficients. Following our analysis, we find that while the speed-dependent variations of the apparent recovery rates observed with narrow-band probing can vary by up to a factor of 2 depending on the detuning, our best estimates of the thermally averaged total RET rates remain significantly smaller than those of Fei et al.^{37,43} and display a qualitatively different trend with rotational state in the case of He only.

The previous comparisons of experiment and theory for He + CN ($X^2\Sigma^+$) collisions highlighted the even-odd alternation in state-to-state rate constants, noting a better agreement at higher rotational states, and speculating that the differences observed at lower rotational states could be attributed to deficiencies in the potential.⁴⁵ To compare total rotationally inelastic rate constants from selected initial states, we have summed over final states of the calculated state-to-state thermal rate constants, as tabulated in the supplemental information of Lique et al.⁴⁵ These

calculated total removal rate constants indeed show much better agreement with the present depletion recovery measurements than with the SEP/LIF measurements. The final column of Table 1 shows these total RET rate coefficients from the Hibridon calculations of Lique et al.⁴⁵ and Figure 7 summarizes the rotational state dependence of total inelastic rate constants for CN ($X^2\Sigma^+$) with He from multiple investigations, including our own quasi-classical trajectory studies, extended to higher rotational levels, briefly described in the following section. Figure 8 makes a similar comparison for the case of Ar collisions, including new quantum scattering calculations performed as part of this work. (For details on these calculations, see the Supplementary Information.)

We are led to suspect that the SEP/LIF rates^{37,43} may be overestimated due to an unrecognized contribution by the photolytic precursor, particularly so for the lower rotational states. The SEP/LIF rates were calculated from one concentration, typically 3.5%, of C_2N_2 and a single pressure, neglecting possible contributions of the precursor to the total decay rate. While C_2N_2 is unlikely to be as efficient as our precursor, CH_3COCN , at enhancing the total RET rates, we note that we would substantially overestimate of the recovery rate constant, particularly for low rotational states, if we simply divided the observed rate by the partial pressure of He or Ar for 3.5% mixtures, rather than evaluating the slope with respect to the He or Ar partial pressure. We are no longer able to procure C_2N_2 for tests in our laboratory, although previous RET measurements⁴⁶ of CN ($B^2\Sigma^+$) with He and C_2N_2 collision partners show total RET rate constants nearly independent of rotational states for He, while the C_2N_2 rate constants were larger and strongly increasing at lower rotational states, a pattern qualitatively similar to what we observe for He and CH_3COCN collisions with CN ($X^2\Sigma^+$). Earlier studies in the Wittig laboratory of rotational relaxation from very high rotational states of CN ($X^2\Sigma^+$) pointed to a

qualitative difference between He and Ar as a collision partner.⁴⁷ Following 193 nm photodissociation of BrCN, rotational levels of CN above 50 were found to be metastable in Ar, yet efficiently thermalized by He, indicating that the RET rates fall off at high rotational states much more slowly for He than for Ar collisions.⁴⁷

Modelers who use experimental or theoretical energy transfer rate constants in astrophysics,⁴⁸ combustion diagnostics, and non-thermal plasma diagnostics⁴⁹ should be alert to these new rate constants, which appear fully consistent with the quantum scattering calculations.

4.2 Kinematic differences between Ar and He collision partners. Following many investigations into rotational energy transfer, a general trend for high rotational states to become increasingly resistant to state-changing collisions is expected, as the minimum energy gap between rotational states increases.^{50,51} Adiabaticity arguments can be invoked: as the time scale for rotation decreases relative to the timescale of the collisional encounter, a collisionally sudden limit at low rotation evolves toward a rotationally averaged and thus more isotropic interaction at high rotational states, suppressing the inelastic probabilities.^{9,51,52} In qualitative terms, the slower Ar collisions should reach this region of decreasing rotationally inelastic cross sections at lower rotational states than for He collisions, yet the rate constants must eventually decrease for thermal He collisions at high enough rotational states. Quantitatively, the details of the interaction potential will also matter. The excellent agreement between our experimental rates and the quantum scattering calculations on an *ab initio* surface with frozen CN bond length should not be surprising, but the scattering calculations are silent on the question of dynamics vs. kinematics, *i.e.*, the relative importance of the interaction potential and the mass combinations. Is the modest difference in the interaction potential for Ar and He interaction with CN ($X^2\Sigma^+$) at all important, or can the effects be primarily attributed simply to the differences in collision

timescales? The dramatic differences between He and Ar observed by Hay et al.⁴⁷ in the relaxation of very high rotational states of CN ($X^2\Sigma^+$) encouraged us to explore the behavior at higher rotational levels.

Most features of RET are well described by quasi-classical trajectory (QCT) methods,^{53,54,55} which do not suffer from rapidly increasing computational effort at high energies and high angular momentum states. We therefore implemented a classical rigid rotor trajectory program⁵⁶ to explore independent effects of the reduced mass and the potential in this RET process. A brief description of the QCT calculations is included in the Supplemental Information. Comparisons were made between total rotationally inelastic rate constants as a function of initial rotational level for CN ($X^2\Sigma^+$) + He and hypothetical systems with the same potential⁴⁵ but replacing the mass of He with the mass of Ne or Ar. Another set of calculations used a CN ($X^2\Sigma^+$) + Ar potential²⁰ with the collider mass again chosen from the masses of He, Ne and Ar. The calculations with realistic masses for both the CN + He and CN + Ar cases agree very well with the quantum scattering calculations on the same potentials for initial rotational states $N < 18$, if the threshold angular momentum change for classifying collisions as inelastic is set to $\pm \hbar$.

The continuation to higher initial rotational levels that were not considered in the quantum scattering calculations can be seen as calculated QCT points in Figures 7 and 8. A continuously decreasing inelastic rate constant with increasing rotation is seen for Ar, as expected, while He shows a nearly flat region between $N=3$ and 20 before beginning a more gradual decrease in rate constant at higher initial rotational states. Artificially changing the interaction potential from CN ($X^2\Sigma^+$) + He to the CN ($X^2\Sigma^+$) + Ar potential, while keeping the collider mass fixed at 4 nearly doubles the rate constants but without significantly changing the rotational state dependence of

the rate. The doubling of the rate constant is primarily due to the larger repulsive radius of Ar compared to He, which increases the cross sections accordingly. Comparing the same two potentials with the mass fixed at 40 shows a different rotational state dependence, falling off more steeply at high rotational levels, but again with a state dependence independent of the mass, but with the overall rates approximately doubled in the CN ($X^2\Sigma^+$) + Ar potential. When comparing the real CN ($X^2\Sigma^+$) + Ar system with the real CN ($X^2\Sigma^+$) + He system, the increase in the cross sections is compensated by the reduction in the mean relative velocities to make the rate constants similar. In this case, where the interaction potentials have similar repulsive gradients and only weakly attractive van der Waals minima, differing mostly in the range of the repulsive wall, the QCT studies support the view that kinematic effects are dominant in such atom-diatom inelastic encounters.⁵⁷

4.3 Speed Dependent Effects in energy transfer

The relaxation rate at a given Doppler shift can be described as a non-thermal average over the speed-dependent inelastic cross section, with the relative velocity distribution biased by one Doppler-selected velocity component of the probed species. For a Doppler-selected velocity group of the absorbing molecule CN with a specific Doppler shift corresponding to z-component of velocity for the absorber v_z the conditional probability of relative collision velocity v_r is given by¹⁹

$$f(v_r | v_z) = 2 \frac{v_r \sqrt{\alpha}}{v_0^2 \sqrt{\pi}} \exp\left(-\frac{v_r^2}{v_0^2}\right) \times \int_{-v_r}^{v_r} \exp\left[\frac{u^2 - \alpha(v_z - u)^2}{v_0^2}\right] du \quad (8)$$

where $v_0 = [2kT(m_a + m_p)/m_a m_p]^{1/2} \equiv \sqrt{2kT/\mu}$ is the most probable relative velocity at temperature T ; m_a and m_p are the masses of the absorber (CN) and the perturber (He or Ar), and

$\alpha = 1 + m_p/m_a$ (correcting a typographical error in reference [19], in which m_p and m_a were reversed). An equivalent expression for the conditional collision velocity was given by Smith, et al.⁹ which has been used for the analysis of Doppler-selected excitation studies:

$$f(v_r | v_z) = \frac{v_r}{2\sqrt{1+r}} \exp\left(\frac{-[v_r^2 - (1+r)v_z^2]}{2(1+r)}\right) \times \left[\operatorname{erf}\left(\frac{v_r + (1+r)v_z}{\sqrt{2r(1+r)}}\right) + \operatorname{erf}\left(\frac{v_r - (1+r)v_z}{\sqrt{2r(1+r)}}\right) \right], \quad (9)$$

with $r = m_a/m_p$ and both v_r and v_z normalized to a reference speed of $\sqrt{kT/m_a}$, (correcting a typographical error in the argument to the exponential function in Eq. 3a of ref 9).

The Doppler-selected rate at temperature T will then vary with the Doppler shift according to

$$k(v_z) = \int_0^\infty v_r \sigma(v_r) f(v_r | v_z) dv_r \quad (10)$$

where $\sigma(v_r)$ is the rotationally inelastic cross section for a relative velocity v_r . To compare with the measured Doppler-resolved relaxation rates, we can use Eq. 10 to perform non-thermal averages of the speed-dependent cross sections from the quantum scattering calculations, as outlined in the Supplementary Information. Figure 9a illustrates the calculated speed-dependent total rotationally inelastic cross sections for three of the rotational states measured in this work. Performing the non-thermal averages using Eq. 10 gives theoretical curves for the corresponding Doppler-resolved relaxation rates, for selected rotational states of CN ($X^2\Sigma^+$, $v = 0$) colliding with Ar, illustrated as solid lines in Figure 9b.

Despite the substantially different forms of the speed-dependent cross sections, after averaging, the Doppler-shift resolved rates have a less distinctive variation, all of which can be quite well described by the empirical form of Eq. 2, used in the fitting of experimental data. The dashed lines superimposed on the numerical non-thermal averaged rates in Figure 9b are the best-fit representations of the calculated Doppler-shift resolved rates adjusting k_0 and b to

represent the rates for probed Doppler shifts up to 1500 m/s. Table 4 summarizes the theoretical values of k_0 and b determined in this way from the non-thermal averages of total rotationally inelastic rates of selected rotational states of CN ($X^2\Sigma^+$) in collision with Ar and with He. As expected, the speed-dependence, parameterized by b is smaller for He than for Ar. The rotational state dependence of b reflects a variation in the shape of the speed-dependent cross sections. The values of k_0 are less than the unbiased thermal rate constants, by 10-15% in Ar, and a smaller margin in He.

Some qualitative features of these results can be compared to experiment, although the experimental measurement of the Doppler-resolved saturation recovery rates, as illustrated in Supplemental Figures S4 and S5 are noisy and affected by additional factors not included in the quantum scattering calculations. The error bars shown in the figures are 1 σ statistical errors from the global fits, but the scatter with respect to variations in pressure and rotational state indicates additional systematic errors associated with extracting second-order effects from imperfect data. There is a general trend toward larger b values at lower rare gas pressures, as the precursor concentration is increasing and contributes disproportionately to the observed speed-dependence. At the lower concentrations of precursor (higher total pressure), the trend toward smaller b values for He collisions compared to Ar is confirmed, as the selected CN velocity makes less of a contribution to the total relative velocity for collisions with light targets. Only the extrapolation to high dilution gives the intrinsic rare gas speed-dependence, and at the high pressure, high dilution end of our measurement range the absolute rates are faster, closer to our limiting time resolution, making our determination of the speed dependence more uncertain there.

A final and subtle complication in the interpretation of the Doppler-shift dependent saturation recovery rates is the influence of velocity-changing collisions. The molecules probed at a specific Doppler detuning will have an instantaneous velocity component along the probe beam direction selected by the laser frequency. In the presence of velocity randomizing collisions, however, the probed velocity groups are not persistent and uncoupled, and the relaxation rate will include not only the velocity-averaged inelastic rate of the probed velocity group, but also any net growth or decay due to velocity changing collisions, even during the time corresponding to a small fraction of the first inelastic collision. The competition between elastic and inelastic collisions with both rare gas and a precursor can add significant complexity to the concentration dependence and initial state dependence of the Doppler-resolved relaxation rates. The more effectively velocity randomization competes with inelastic collisions, the less deviation from thermal Gaussian line shapes will occur during the population thermalization, and the recovery rate will be more independent of the Doppler shift, leading to reduced values of b . The calculated non-thermal average recovery rates using Eq. 10 should thus be considered upper bounds to the speed-dependence, obtained by neglecting the effects of velocity-changing collisions. When experimental values of b exceed the theoretical values, we suspect a continued contribution from inelastic collisions with the heavy precursor. Future experiments measuring narrow-band saturation recovery kinetics following sub-Doppler hole burning should distinguish between inelastic and elastic velocity-changing collisions that contribute to the spectral evolution of the depletion signal.

5. Conclusions

This work demonstrates the use of transient FM spectroscopy to measure ground state depletion recovery kinetics in thermal gas phase samples containing CN radicals. Polarized absorption signals can be measured with sufficient dynamic range and fidelity to determine thermal rate constants for rotational energy transfer at pressures low enough to access the single-collision time scale. Total rotationally inelastic rate constants show a dependence on the initial rotational state that is surprisingly different for collisions of CN(X) with He vs. Ar, in contrast to some previously reported experiments, but in good agreement with quantum scattering calculations.

Fast processes that compete effectively with velocity thermalization will be characterized by variable kinetics that depend on the Doppler detuning of a narrow band probe laser. Even when the initial pulsed perturbation to an initially thermalized system is performed with unbiased velocity selection, the Doppler-resolved probe process reveals speed-dependent reaction rates and a spontaneous cooling of the translational distribution, until velocity-changing collisions reestablish the Maxwell-Boltzmann velocity distribution at the ambient temperature. The visibility of the speed-dependent kinetic signature will depend on the mass ratio of the probed molecule and the collision partner, the variation of the cross section with the collision velocity, and the competition with elastic velocity-randomizing collisions.

Table 1.Total rotationally inelastic rate constants* for CN ($X \ ^2\Sigma^+$) + He

Initial N	F ₁ /F ₂	k _{RET} ^a	k _{RET} ^b	SEP/LIF ($\nu=2$) ^c (unresolved F ₁ +F ₂)	Calculated ^d
0	F ₁	2.8 (2)	3.0(2)		3.17
4	F ₂	1.9 (2)	2.1(3)	4.00(20)	2.73
4	F ₁	2.0(2)	2.1(3)		2.71
6	F ₂	2.5(1)	2.6(1)		2.7
10	F ₂	2.3(1)	2.4(2)		2.63
11				3.61(10)	2.6
13	F ₁	2.3(1)	2.5(2)		2.53
17	F ₁	2.4(1)	2.5(1)		2.37
24				3.06(18)	
31				2.07(16)	

* Rate constants in units of $10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.a. Rate constants based on pressure dependence of single exponential fits to early time thermal population fits. The numbers in parentheses represent 1σ statistical uncertainties in the preceding digits.

b. Rate constants based on pressure dependence of 298 K average of velocity-dependent initial rates from global fits to spectral data during the first two time constants of decay.

c. From ref [37], assuming 300 K for conversion from $(\text{Torr}\cdot\text{ns})^{-1}$ d. Quantum scattering calculations⁴⁵ using Hibridon code.⁵⁸

Table 2.Total rotationally inelastic rate constants* for CN ($X^2\Sigma^+$) + Ar

Initial N	F ₁ /F ₂	k _{RET} ^a	k _{RET} ^b	SEP/LIF ($\nu=2$) ^c (unresolved F ₁ +F ₂)	Calculated ^d
0	F ₁	3.9(2)	4.2(2)		4.73
4	F ₂	2.5(2)	2.8(3)	5.24(15)	3.51
4	F ₁	2.6(2)	2.9(3)		3.47
6	F ₂	2.5(2)	2.8(2)		3.12
10	F ₂	2.3(2)	2.4 (2)		2.72
11				4.06(31)	2.60
13	F ₁	2.1(1)	2.2(2)		2.35
17	F ₁	1.6(1)	1.6(1)		1.81
24				2.42(46)	
31				2.11(25)	

* Total removal (recovery) rate constants in units of $10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.a. Rate constants based on pressure dependence of single exponential fits to early time thermal population fits. The numbers in parentheses represent 1σ statistical uncertainties in the preceding digits.

b. Rate constants based on pressure dependence of 298 K average of velocity-dependent initial rates from global fits to spectral data during the first two time constants of decay.

c. From ref [43], assuming 300 K for conversion from $(\text{Torr}\cdot\text{ns})^{-1}$ d. This work, quantum scattering calculations using Hibridon code⁵⁸

Table 3.

Total rotationally inelastic rate constants* for CN ($X^2\Sigma^+$) + CH₃COCN

N	F_1/F_2	$k_{\text{RET}}^{\text{a}}$	$k_{\text{RET}}^{\text{b}}$
0	F_1	95(5)	78(3)
4	F_2	75(8)	--
4	F_1	80(7)	--
6	F_2	43(3)	34 (1)
10	F_2	32(4)	--
13	F_1	25(4)	--
17	F_1	19(3)	8.2(6)

* Rate constants in units of $10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. The numbers in parentheses represent 1σ statistical uncertainties in the preceding digits.

^aDerived from common intercepts of He and Ar dependent rates at 10 mTorr CH₃COCN

^bDerived from CH₃COCN pressure dependence of initial recovery rates at fixed 100 mTorr Ar

Table 4.

Theoretical Doppler-shift dependence of total rotationally inelastic rate constants for selected rotational states of CN ($X^2\Sigma^+$) + Ar and He, at 298 K. Fit to $k(x_D) = k_0\sqrt{1+bx_D^2}$.

N (F_1)	Helium		Argon	
	k_0 ($10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	b	k_0 ($10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	b
0	3.08	0.083	4.66	0.145
2	2.68	0.092	3.92	0.190
4	2.63	0.090	3.31	0.272
6	2.61	0.089	2.89	0.334
8	2.59	0.089	2.68	0.349
10	2.54	0.091	2.49	0.379
12	2.49	0.095	2.25	0.447
14	2.41	0.100	1.97	0.573
16	2.33	0.105	1.66	0.780

Supporting Information

S1. Temperature Dependence of FM Line Shapes

S2. Quantum Scattering Calculations of Rotationally Inelastic Collisions of CN(X) by Rare Gases

S3. Quasi-Classical Trajectory Calculations of Rotationally Inelastic Collision of CN(X) by Rare Gases

S4. Supplemental Figures S4 and S5, illustrating pressure-dependent values of speed-dependent relaxation parameters b for He and Ar and an assortment of CN rotational states.

This material is available free of charge via the Internet at <http://pubs.acs.org>

Author's Contributions

DF performed most of the experimental work, analyzed the data, and performed the QCT calculations. Preliminary versions of the experimental work and analysis were done by MLH. HGY provided code and consultations on the QCT calculations. PJD performed the quantum scattering calculations, wrote the corresponding sections of the paper, and participated in discussions of the work. TJS participated in planning and discussions of the work. GEH designed the experiments, participated in the analysis and wrote most of the paper. All authors have given approval to the final version of the manuscript.

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Figure Captions

Figure 1. Experimental block diagram for FM-detected saturation recovery kinetics. cw probe: Ar⁺ pumped Ti:sapphire laser; ns bleach: Nd:YAG-pumped dye laser; EOM: electro-optic phase modulator; PEM: photoelastic polarization modulator; DSO: digital storage oscilloscope; ϕ shift: voltage controlled phase-shifter.

Figure 2. Typical transient FM signal with saturation recovery kinetics. Signal is observed at 10895.484 cm^{-1} , near the peak of the FM signal for the CN $P_2(6)$ line in the (1-0) band for a sample of 10 mTorr CH_3COCN and 590 mT Ar. Photolysis laser fires 12 μs before $t=0$, when the bleach laser fires. The bleach laser is tuned to the center of the $P_2(6)$ line in the (4-0) band at 16103.64 cm^{-1} . Inset: expanded saturation transient, expressed as fractional depletion vs. time for a single polarization. Solid line fit: single exponential with final offset.

Figure 3. Thermal fits to FM depletion signals at selected times following bleach laser pulse. Symbols depict transient FM depletion data, polarization averaged, and optimally rotated to isolate absorption- and dispersion-phase spectra. Solid lines illustrate best-fit absorption (A_{FM}) and dispersion (D_{FM}) thermal lineshapes, with an adjustable temperature, Doppler-integrated intensity, and phase angle for each time slice. This example is for a sample containing 10 mTorr CH_3COCN and 590 mTorr Ar, probed and bleached on a $R_1(0)$ line.

Figure 4. Time slice fits to total depletion and translational temperature for the same sample illustrated in Figure 3. a) translational temperature vs. time after saturation, showing rapid cooling and slow reheating; b) Doppler-integrated depletion amplitude, normalized to initial value; c) semi-logarithmic plot of the same data shown in b).

Figure 5. Variation in the observed decay kinetics at selected Doppler detunings for the $P_2(4)$ line, with 190 mTorr Ar added to 10 mTorr CH_3COCN . The full frequency-dependent decay was treated with a global fit; FM decay curves are shown here at Doppler detunings of $x_D = \pm 0.65$ (average signals near the + and - peak FM signals, about $\pm 0.010 \text{ cm}^{-1}$ from line center) and $x_D = \pm 1.5$ (average of signals about $\pm 0.024 \text{ cm}^{-1}$ from line center, where the FM signal intensity has dropped to about one half of the maximum). Solid lines are the corresponding frequency-selected decay kinetics from the global fit, normalized to the same initial depletion. Measured decay signals (symbols) have been scaled by the same normalization factors as the fits.

Figure 6. Pressure dependence of initial recovery rates for selected rotational states in He and Ar. The CH_3COCN precursor partial pressure was maintained at 10 mTorr, contributing a strong rotational state dependence to the intercepts.

Figure 7. Total RET rate constants for $\text{CN}(X^2\Sigma^+) + \text{He}$ vs. initial rotational state. Open symbols are 295 K thermal rate constants, summed over all inelastic channels from the Hibridon scattering calculations of Lique, et al.⁴⁵ Blue squares are the SEP/LIF total removal rate constants from Fei et al.³⁷ converted from $(\text{ns}\cdot\text{Torr})^{-1}$ units, assuming 300 K ideal gas density. Red triangles labeled FM are this work, based on the global fits described in the text. Points and connecting lines are from quasi-classical trajectory calculations for total inelastic rate constants, (this work).

Figure 8. Total RET rate constants for $\text{CN}(X^2\Sigma^+) + \text{Ar}$ vs. initial rotational state. Open symbols are 298 K thermal rate constants, summed over all inelastic channels from the Hibridon scattering calculations (this work). Blue squares are the SEP/LIF total removal rate constants from Fei et al.⁴³ converted from $(\text{ns}\cdot\text{Torr})^{-1}$ units, assuming 300 K ideal gas density. Red

triangles labeled FM are this work, based on the global fits described in the text. Points and connecting lines are from quasi-classical trajectory calculations for total inelastic rate constants (this work).

Figure 9. (a) Speed-dependent rotationally inelastic cross sections for $\text{Ar} + \text{CN} (X^2\Sigma^+)$ in selected initial rotational states, from quantum scattering calculations. (b) Doppler-resolved total inelastic rate for selected initial rotational states, using Eq. 10 to average $v_r \sigma(v_r)$ over $f(v_r | v_z)$, the conditional relative velocity given the Doppler shift. Solid lines are the numerical non-thermal averages. Dashed lines are best fits to empirical form $k(x_D) = k_0 \sqrt{1 + bx_D}$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

TOC-Graphic

Supplemental Information: Doppler-Resolved Kinetics of Saturation Recovery

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Supplement 1. Temperature dependence of FM line shapes

Frequency modulated line shapes of thermal, Doppler-broadened lines are more sensitive to the temperature than are direct absorption line shapes. A simple example illustrates this. Consider a Doppler broadened Gaussian absorption line at a reference temperature of 300 K, with a unit maximum intensity, plotted on a normalized frequency axis, $x_D = (\omega - \omega_0)/\omega_D$, where $\omega_D = \omega_0 \sqrt{2k_B T/m}/c$ is the Doppler shift at the most probable velocity:

$$A(x_D) = e^{-x_D^2}. \quad (\text{S1})$$

Cooling to 250 K with no change in density will increase the peak amplitude and decrease the line width by a factor of $\sqrt{300/250}$, when plotted against the same 300 K normalized frequency, as shown in Fig S1a.

For a RF modulation frequency 0.4 times the Doppler shift of the most likely thermal velocity at 300K, ($x_{RF} = 0.4$), typical of our current experiments, the corresponding FM line shape in the absorption phase will be a difference of frequency offset Gaussians, as shown in Fig S1b according to Equation S2 (neglecting the effects of second-order sidebands):

$$A_{FM}(x_D) = A(x_D + x_{RF}) - A(x_D - x_{RF}). \quad (\text{S2})$$

Figure S1. Normalized direct absorption (a) and absorption phase FM signals (b) for a fixed total population at 300 K and 250 K. A modulation frequency 0.4 times the Doppler shift at the most likely velocity is used for this example.

The intensity of the colder FM spectrum exceeds that of the warmer sample over a wider range of detunings, and by a larger factor, compared to direct absorption. Figure S2 shows the ratio of signal intensity at 250 K relative to 300 K as a function of Doppler detuning for these example direct absorption and FM line shapes.

Figure S2. Relative intensity of 300 K vs. 250 K signals as a function of detuning for direct absorption and absorption phase FM monitoring.

The warning to be drawn from this illustration is that when monitoring a population by narrow-band direct absorption (or LIF) measurements, if the temperature cools from 300 K to 250 K during the first decay lifetime, $1/k$, of a single exponential decay, the initial apparent decay rate will be reduced by about 9% at line center, and be approximately undistorted at a detuning of $x_D = \pm 0.68$, near the detuning of half-maximum. At larger Doppler shifts, the apparent decay rate will exceed the thermally averaged decay rate by an increasing margin. Analyzing the decay rate of the Doppler integrated area rather than the decay at line center is a common and sensible treatment for such heterogeneous speed-dependent kinetics.

For FM spectroscopy, the trend is the same, but the discrepancy is larger. Near line center (where the FM signal vanishes) the apparent decay rate will be reduced by more than 20%, and it will remain slower than the thermally averaged decay rate at all detunings $|x_D| \leq 1.28$. When the speed distribution is changing along with the total population, kinetic measurements at fixed frequency can be subject to systematic error, and an analysis that explicitly considers the time-

dependent line shape is required for accurate kinetic interpretation, as has been implemented in sections 3.2 and 3.3 of the main paper.

Supplement 2. Quantum Scattering Calculations of Rotationally Inelastic Collisions of CN(X) by Rare Gases

The HIBRIDON suite of programs¹ was employed to carry out close-coupling calculations of state-to-state integral cross sections vs. collision energy for collision of CN(X) with argon. The CN(X, $v=0$)–Ar interaction potential, taken from ref 2, was parameterized as a table of Legendre expansion coefficients $V_\lambda(R)$:

$$V(R, \theta) = \sum_{\lambda=0}^{10} V_\lambda P_\lambda(\cos \theta), \quad (\text{S3})$$

where the CN bond length is fixed at the $v = 0$ average value, R and θ are the other two Jacobi coordinates and $P_\lambda(\cos \theta)$ is a Legendre polynomial. The angular expansion coefficients V_λ on a grid of R values can be generated from routines and data files included in the current download of HIBRIDON.¹

Convergence of the cross sections was checked with respect to the size of the rotational basis and the number of partial waves, and these varied as a function of the total energy. At the highest energy considered (2000 cm^{-1}), the rotational basis included all levels with $j \leq 22.5$, and the scattering calculations included all total angular momenta $J \leq 500.5$.

Total removal cross sections for a given rotational level as a function of collision energy were determined by summing all the state-to-state integral cross sections for transitions out of that level. For the calculation of thermal rate constants, the cross sections were computed on a grid of collision energies, up to a total energy of 2000 cm^{-1} and were averaged over a room-temperature (298 K) Maxwellian distribution of relative velocities.³

Supplement 3. Quasi-Classical Trajectory calculations of rotationally inelastic scattering in CN(X) by rare gases.

Classical equations of motion were integrated to investigate the rotationally inelastic scattering of a rigid CN molecule by a rare gas atom, following standard procedures.^{4,5,6} The diatomic bond length was constrained to be rigid by the method of Lagrange.⁴ The CN(X,v=0)–Ar interaction potential² was the same as was used in the quantum scattering calculations of this work, and the CN(X,v=0)–He potential⁷ was in the same form of an R-dependent Legendre expansion. Both potentials can also be generated using routines and data files included in the current download of Hibridon.¹ The initial angular momentum of the CN rotor was fixed for each set of trajectories, while the plane of rotation and initial rotational phase were chosen at random, relative to the initial atomic velocity, while the initial impact parameter, b , was set to $b_{\max}$ times the square root of a random uniform number between 0 and 1. The maximum impact parameter, $b_{\max}$, was chosen large enough to include all rotationally inelastic collisions, based on a small preliminary set of calculations for each initial rotational state and collision partner. The relative velocities were sampled from a Maxwell-Boltzmann speed distribution at 298 K. A split step Verlet integrator was used,⁸ with a full time step of ~ 0.2 fs, typically conserving total energy within 0.1%. Trajectories were started at a separation of $20 a_0$ and terminated when the separation exceeded $20 a_0$. Batches of 50,000 to 500,000 trajectories were run for each initial rotational state investigated. If the angular momentum is conventionally⁵ binned by rounding the final classical angular momentum into the nearest integer multiple of $\hbar$, the total rotationally inelastic rate constants are found to exceed the quantum mechanical scattering results and the experimental values by about 30%, while very accurately matching the shape of the rotational

state dependence computed by quantum scattering calculations on the same potential. If instead, the threshold for classifying a collision as rotationally inelastic is assigned as a change of at least $\pm \hbar$, the computed total inelastic cross sections and rate constants are smaller and in excellent agreement with both quantum scattering and experimental values where they are available. Figures 6 and 7 in the main paper includes these QCT calculated rate constants for an extended range of rotational states, along with experimental and quantum calculations at lower rotational states. This method can then be considered a way of extrapolating the inelastic rate constants to higher initial rotational states, where the quantum scattering calculations become increasingly demanding, and the classical results should be reliable.

To investigate the relative effects of the potential and the mass of the collider, a series of artificial combinations of potential and mass were compared, using the Ar and He potentials in combination with the mass of He, Ne and Ar. Figure S3 summarizes these results, collecting the three different masses for fixed potential in each panel of the plot. It can be seen that changing the potential from He to Ar at fixed mass approximately doubles the rate, without changing the shape of the rotational state dependence significantly. Increasing the mass leads to a steeper reduction in the total inelastic rates from higher initial rotational states regardless of the choice of potential. In this comparison of two generally quite similar potentials, the mass effect is clearly dominant.

Figure S3. Calculated rotational state dependence of thermal rate constants for total rotationally inelastic collisions of CN ($X^2\Sigma^+$, $v=0$) for artificially modified atomic mass of the collider M, using QCT. Masses $m=4$, 20, 40 chosen to represent He, Ne and Ar. Top panel: calculations using the CN + Ar potential; Bottom panel: calculations using CN + He potential. QM: blue lines represent corresponding quantum mechanical scattering calculations for He from Lique et al.⁷ and for Ar from this work.

S4. Supplemental Figures

Figure S4. Helium pressure-dependent speed-dependent parameter b for a selection of CN rotational states; CH_3COCN partial pressure is 10 mTorr for all samples, and contributes disproportionately to the speed dependence at low total pressures.

Figure S5. Argon pressure-dependent speed-dependent parameter b for a selection of CN rotational states; CH_3COCN partial pressure is 10 mTorr for all samples, and contributes disproportionately to the speed-dependence at low total pressures.

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