Temperature-dependent phonon-induced relaxation of the nitrogen-vacancy spin triplet in diamond

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Phonon-induced relaxation within the nitrogen-vacancy (NV) center’s electronic ground-state spin triplet limits its coherence times, and thereby impacts its performance in quantum applications. We report measurements of the relaxation rates on the NV center’s $|m_s = 0 \rangle \leftrightarrow |m_s = \pm 1 \rangle$ and $|m_s = -1 \rangle \leftrightarrow |m_s = +1 \rangle$ transitions as a function of temperature from 9 to 474 K in high-purity samples. Informed by ab initio calculations, we demonstrate that NV spin-phonon relaxation can be completely explained by the effect of second-order interactions with two distinct groups of quasilocalized phonons. Using a novel analytical model based on this understanding, we determine that the quasilocalized phonon groups are centered at 68.2(17) and 167(12) meV.

Introduction.—The nitrogen-vacancy (NV) center is a point defect in diamond that has become a promising platform for quantum technologies ranging from nanoscale magnetic resonance imaging [1, 2] and electric field sensing [3, 4] to quantum information processing [5–7]. The NV center owes much of its appeal to its crystalline host, which allows the system to be placed near other materials or integrated into larger devices without the need for trapping or cooling [8, 9]. Despite these compelling advantages, the NV center’s solid-state environment also presents significant challenges. In particular, relaxation driven by spin-phonon interactions fundamentally limits the system’s achievable electronic spin coherence times and therefore its performance in quantum applications. Accordingly, several works have explored the temperature dependence of phonon-limited relaxation on the single-quantum transition between the $|m_s = 0 \rangle$ and $|m_s = \pm 1 \rangle$ levels of the NV’s ground-state electronic spin triplet [10–13]. However, although relaxation on the double-quantum transition between the $|m_s = -1 \rangle$ and $|m_s = +1 \rangle$ levels also places limits on NV center coherence times, phonon-limited relaxation on this transition has not been systematically characterized, leaving the maximum achievable NV coherence times unknown for a wide temperature range.

To our knowledge, the only systematic measurements of phonon-limited double-quantum relaxation to date are Refs. [14] and [15]. In Ref. [14], we found that double-quantum relaxation occurs roughly twice as fast as single-quantum relaxation in the phonon-limited regime at room temperature. In Ref. [15], Lin et al. present measurements of the single- and double-quantum relaxation rates from room temperature up to 600 K, but several discrepancies of the measured rates with prior works suggest that these results cannot be easily generalized to describe NV spin-phonon relaxation in high-purity samples. (See Supplemental Material [16] for analysis of Ref. [15] in the context of prior results.) The temperature dependence of phonon-limited relaxation on the double-quantum transition has not previously been characterized below room temperature.

In this Letter, we present measurements of the temperature dependence of the single- and double-quantum relaxation rates of the nitrogen-vacancy center’s electronic ground-state spin triplet in high-purity samples from 9 to 474 K. We calculate the NV spin-phonon spectral function from first principles and show that its key characteristics provide a complete explanation of NV spin-phonon relaxation at temperatures above which single-phonon processes are negligible. The spectral function reveals that NVs scatter phonons predominantly via second-order spin-phonon interactions, and that the most active phonon modes belong to two vibrational resonances. Informed by the ab initio results, we develop an analytical model of NV spin-phonon relaxation in which transitions are driven by two strongly coupled effective phonon modes at energies of 68.2(17) and 167(12) meV. Additionally, we use our experimental results to calculate the temperature-dependent limits to NV electron spin coherence times imposed by spin-phonon relaxation for super-
positions in both the single- and double-quantum subspaces, and we compare these limits to the longest coherence times reported in literature. Finally, we discuss the relevance of these results to other solid-state defects as well as prospects for mitigating phonon-induced decoherence.

Experimental methods.—Figure 1a shows the level structure of the NV’s ground-state electronic spin triplet, where we abbreviate $|m_s = 0\rangle$ to $|0\rangle$ and $|m_s = \pm 1\rangle$ to $|\pm 1\rangle$. Relaxation on the $|0\rangle \leftrightarrow |\pm 1\rangle$ single-quantum transitions occurs at a common rate $\Omega$; relaxation on the $|−1\rangle \leftrightarrow |+1\rangle$ double-quantum transition occurs at rate $\gamma$. Prior studies of phonon-limited spin relaxation in NVs have focused on the lifetime of $|0\rangle$ under the assumption that $|0\rangle$ and either $|−1\rangle$ or $|+1\rangle$ can be considered a qubit and the third level of the spin triplet can be neglected, tacitly assuming $\gamma = 0$ [10–13]. In these contexts the lifetime of $|0\rangle$ is denoted $T_1$.

The experimental methodology we employ to measure $\gamma$ and $\Omega$ is similar to that used in prior works [14, 17, 18]. Optical polarization and state-selective $\pi$ pulses enable initialization into any spin state. Following a relaxation time $\tau$, the population in a target state is mapped to $|0\rangle$ and read out optically. Differences between pairs of the measured relaxation curves yield single-exponential decays from which the rates $\Omega$ and $\gamma$ are extracted (Fig. 1b) [17, 18]. Experiments are conducted using a homebuilt confocal microscope with support for low-temperature (9 K to ambient) and high-temperature (ambient to 474 K) operation modes (Fig. 1c). Temperature control is provided by an attocube attoDRY800 closed-cycle cryostat in low-temperature mode and a homebuilt copper hot plate in high-temperature mode. A static magnetic field oriented to within approximately $5^\circ$ of the NV orientation under study is applied with a permanent magnet to lift the $|\pm 1\rangle$ degeneracy by $\Delta_\pm \approx 145\text{ MHz}$. Experiments are conducted using two diamond samples which display NV concentrations of 1 ppb (sample A) and $10^{-3}$ ppb (sample B). Further experimental details are available in the Supplemental Material [16].

Results.—Figure 2 displays measurements of the relaxation rates $\Omega$ and $\gamma$ as functions of temperature between 9 and 474 K for single NV center and NV ensemble measurements in two samples with different defect concentrations. Above 125 K, sample-dependent contributions to $\Omega$ and $\gamma$ fall below 10%, indicating that the relaxation rates are dominated by phonons in the diamond lattice, rather than by interactions with other defects. In Ref. [14], we found that $\gamma \approx 2\Omega$ at room temperature. Our results here demonstrate that this factor of 2 is coincidental rather than fundamental, as the ratio $\gamma/\Omega$ declines monotonically from approximately 2.5 to 1.5 between 200 and 474 K [16].

Prior work has successfully fit the temperature dependence of the single-quantum relaxation rate $\Omega$ using an empirical model in which the high-temperature behavior is characterized by a term that scales with temperature as $T^5$ [10, 12, 13]. Ostensibly, this $T^5$ term may arise due to Raman scattering of low-energy acoustic phonons which are weakly coupled to the spin via first-order interactions, following the process described by Walker in Ref. 19. However, we argue that unlike for other spin systems (e.g. several coordination compounds as recently shown in Ref. 20), first-order spin-phonon interactions provide only negligible contributions to Raman scattering for the NV center in diamond. According to Fermi’s golden rule, the rate of Raman scattering due to first-order interactions scales quadratically with the square of the first-order interaction strength divided by the energy of the virtual state. The first-order interaction strength is roughly $D\Delta u/a$, where $D$ is the zero field splitting, $\Delta u$ is the atomic displacement, and $a$ is the nearest neighbor distance in diamond; the virtual
FIG. 2. Log-log plot of the temperature dependence of spin-phonon induced relaxation rates $\gamma$ and $\Omega$. Error bars are one standard error. At temperatures above 125 K (vertical gray line in inset), contributions from sample-dependent constants are below 10%. Darker lines show fit according to the proposed model described by Eqs. (4) and (5), where dotted (dashed) lines correspond to the sample-dependent constants for sample A (B). Lighter solid lines show relaxation rates predicted by ab initio calculations with no free parameters. For clarity, only data in the phonon-limited regime above 125 K is shown in the main plot. Inset: Reproduction of the main plot with linear axes showing all data collected for this work.

state energy is $\hbar \omega \sim 10$ THz for the acoustic phonon branch in diamond. In contrast, contributions to Raman scattering from second-order interactions scale quadratically with the second-order interaction strength, approximately $D(\Delta u/a)^2$. Thus the ratio between the first-order and second-order contributions is on the order of $(D/\hbar \omega)^2 \sim 10^{-8}$, indicating that Raman scattering due to first-order interactions can be neglected for the NV center and other spin-1 defects in diamond. This suggests the need for a more physically sound model of NV spin-phonon relaxation.

In order to better understand the physical origins of NV spin-phonon relaxation, we develop an ab initio microscopic theory of the relaxation processes. The spin relaxation rate may be expressed [20] as

$$\Gamma = \Gamma_0 + \Gamma_1^{(1)}(T) + \Gamma_1^{(2)}(T) + \Gamma_2^{(1)}(T) + \ldots,$$

where the superscript refers to the order of the spin-phonon interaction (i.e. terms with superscript 1 or 2 are linear or quadratic in the atom displacements respectively) and the subscript refers to the order in perturbation theory. $\Gamma_0$ is a sample-dependent constant term arising from spin-spin interactions with other impurities that only significantly contributes at temperatures below 125 K for high-purity samples and which we do not focus on in this study. $\Gamma_1^{(1)}$ describes the absorption or emission of a single resonant phonon by the spin. Because the energy scale of the NV ground-state triplet is small in comparison to typical phonon energies in diamond, this process is only relevant at subkelvin temperatures [21]. At elevated temperatures, relaxation is dominated by Raman scattering of higher energy phonons.

Two-phonon Raman scattering appears as two different second-order terms in Eq. 1: first-order interactions applied to second order in perturbation theory $\Gamma_1^{(1)}$ and second-order interactions applied to first order in perturbation theory $\Gamma_1^{(2)}$. As discussed above, due to the high frequencies of phonons in diamond, $\Gamma_1^{(1)} \ll \Gamma_1^{(2)}$ for the NV center. Using Fermi’s golden rule, we express the dominant Raman scattering rate as

$$\Gamma_1^{(2)}(m,m')_n(T) = \frac{2\pi}{\hbar} \sum_{ll'} \left| V_{m,m'}^{ll'} \right|^2 \times \left[ n_l(n_l + 1)\delta(\Delta E_) + n_{l'}(n_{l'} + 1)\delta(\Delta E_+) \right]$$

for spin states $|m_s\rangle$ and $|m'_s\rangle$. Here, $V_{m,m'}^{ll'}$ is the matrix element coupling $|m_s\rangle$ to $|m'_s\rangle$ via phonons $l$ and $l'$, and $\Delta E_{\pm} = E_{m'} \pm (\hbar \omega_l - \hbar \omega_{l'}) - E_m$, is the energy difference between the final and initial states of the composite system. The temperature dependence enters via the Bose-Einstein distribution $n_l = [\exp(\hbar \omega_l/k_BT) - 1]^{-1}$. Because typically $E_m, E_{m'} \ll \hbar \omega_l$, we consider only the diagonal $l = l'$ terms moving forward. We avoid a $\delta(0)$ singularity by transforming Eq. (2) into an integral form:

$$\Gamma_1^{(2)}(m,m')_n(T) = \frac{4\pi}{\hbar} \int_0^\infty d(\hbar \omega) \times \left[ n(\omega)[n(\omega) + 1] F_{m,m'}^{(2)}(\hbar \omega, \hbar \omega) \right]$$

where the continuous spectral function $F_{m,m'}^{(2)}(\hbar \omega, \hbar \omega)$ accounts for the phonon density of states and the spin-phonon coupling strengths [16]. We identify the terms $\Gamma_1^{(2)}(\pm 0)$ and $\Gamma_1^{(2)}(\pm \pm)$ as the relaxation rates $\Omega$ and $\gamma$ respectively.

We calculate the diagonal matrix elements $V_{m,m'}^{ll}$ using a plane wave supercell density functional theory simulation package [22, 23] by means of PBE functional [24]. We approximate the spectral function for a macroscopic diamond by taking the convolution of the calculated matrix elements with a normalized Gaussian of variance 7.5 meV (further technical details are given in the Supplemental Material 16). The spectral function displays two distinct peaks near 65 and 155 meV (Fig. 3) which are associated with the phonon modes that change the positions of the carbon dangling bonds [25] and thereby the NV spin density distribution. Evaluating Eq. (3) with the calculated spectral function yields predictions for the spin-phonon relaxation rates with no free parameters that are in rough quantitative agreement with experiment (lighter solid lines, Fig. 2). Above 125 K, we
obtain theoretically predicted relaxation rates that exhibit the same scalings with temperature as the measured rates, with double-quantum relaxation rates that are within 20% of the measured values of $\gamma$ and single-quantum relaxation rates that are approximately 8 times smaller than the measured values of $\Omega$ at room temperature [16]. We hypothesize that the discrepancy in the predicted $\Omega$ is due to the exclusion of combinations of modes for which $l \neq l'$, as combinations of modes with different symmetries likely account for significant matrix elements associated with pairs of different spin operators, which correspond to the single-quantum transitions. As including these off-diagonal combinations is significantly more computationally demanding, we leave their calculation for future work. In addition, we find that the ab initio first-order matrix elements are on the order of 100 MHz, validating the argument that Raman scattering induced by first-order interactions should be negligible for the NV center and other spin-1 defects in diamond [16].

Motivated by our theoretical findings, we propose that the spectral function $F_{m,m'}^{(2)}(\hbar\omega,\hbar\omega)$ may be approximated with just two characteristic energies, resulting in an analytical model of the relaxation rates with two effective phonon modes:

$$\Omega(T) = A_1 n_1(n_1 + 1) + A_2 n_2(n_2 + 1) + A_3(S), \quad (4)$$

$$\gamma(T) = B_1 n_1(n_1 + 1) + B_2 n_2(n_2 + 1) + B_3(S). \quad (5)$$

Here, $n_{1,2} = [\exp(\Delta_{1,2}/k_B T) - 1]^{-1}$ are the mean occupation numbers at the characteristic energies $\Delta_{1,2} = \hbar\omega_{1,2}$, $A_{1,2}$ and $B_{1,2}$ are the coupling coefficients to the effective modes, and $A_3(S)$ and $B_3(S)$ are sample-dependent constants. We find that Eqs. (4) and (5) provide excellent fits to the experimental data (darker lines in Fig. 2) with normalized residuals that are consistent with purely statistical errors [16]. The fit parameters are shown in Table I.

The characteristic energies from the fit are 68.2(17) and 167(12) meV, consistent with the locations of the peaks in the spectral function.

We emphasize that the model of NV spin-phonon relaxation proposed here differs qualitatively from the model used in prior work to describe the temperature dependence of the single-quantum relaxation rate $\Omega$ [10, 12, 13]. Chiefly, our model is physically rooted in ab initio calculations and does not rely on the effect of first-order spin-phonon interactions. In addition, we attribute the high-temperature behavior of the relaxation rates to interactions with a high-energy strongly coupled effective phonon mode, rather than to interactions with the diamond’s low-energy acoustic modes. Although the prior model can be naively extended to provide a good fit to both measured relaxation rates [16], we predict that the prior model will break down at temperatures beyond those reached in this work. We further note that phonon modes with the same energies as those identified here have previously been invoked to describe the major features of the NV center’s optical spectrum [26–28]. We conclude that the model we propose captures NV spin-phonon relaxation physically and empirically; in summary, relaxation is likely dominated by interactions with quasilocalized modes associated with two vibrational resonances near 68 and 167 meV.

**Discussion.**—Phonon-induced relaxation is an incoherent process that places hard limits on the maximum achievable coherence times for superpositions of states within the NV center’s electronic ground-state spin-triplet manifold. Much past work has neglected the effect of $\gamma$ on this limit, and as a result prior expectations for the limits to $T_2$ have likely been overestimates [29, 30]. Including $\gamma$, the maximum relaxation-limited coherence time is

$$T_{2,max}^{(SQ)} = \frac{2}{3\Omega + \gamma} \quad (6)$$

| $A_1$ (s$^{-1}$) | $B_1$ (s$^{-1}$) | $\Delta_1$ (meV) | $A_2$ (s$^{-1}$) | $B_2$ (s$^{-1}$) | $\Delta_2$ (meV) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0.58(8) $\times$ 10$^3$ | 1.51(17) $\times$ 10$^3$ | 68.2(17) | 9(2) $\times$ 10$^3$ | 4.8(14) $\times$ 10$^3$ | 167(12) |

**TABLE I.** Fit parameters for $\Omega$ and $\gamma$ according to the proposed model described by Eqs. (4) and (5). Sample-dependent constants may be found in the Supplemental Material [16]. Uncertainties are 1σ.
for a superposition in the \( \{0\}, \{\pm 1\} \) single-quantum subspace and

\[
\tau_{2,\text{max}}^{(\text{DQ})} = \frac{1}{\Omega + \gamma}. \tag{7}
\]

for a superposition in the \( \{-1\}, \{+1\} \) double-quantum subspace [17, 18]. Fig. 4 shows the relaxation limit in the single-quantum subspace alongside the longest experimentally measured values of \( T_2 \) at various temperatures reported in the literature [29, 31, 32]. Interestingly, we see that the best measured coherence times fall short of the calculated limit despite the inclusion of \( \gamma \). The consistency of the ratio between the measured coherence times and the calculated \( T_{2,\text{max}} \) in the phonon-limited regime (Fig. 4 inset) suggests that the discrepancy may be due to phonon-induced dephasing, an effect which is not included in the definition of \( T_{2,\text{max}} \) [29]. This is consistent with the fact that the \( ab \) initio spectral function associated with dephasing (Fig. 3, black line) has the same two-peak lineshape as the curves associated with relaxation (red and blue lines), and a larger magnitude.

Our results have several implications for future NV research. Because \( T_5^5 \) scales more quickly than \( n(n + 1) \) in the high-temperature limit, we predict that NV spin-phonon relaxation will be slower than expected based on prior work at temperatures exceeding those accessed in this or previous studies. While experimental complexity and fluorescence contrast loss limit most NV applications to temperatures below 700 K, the NV spin can be coherently manipulated even up to 1000 K [33], where we predict relaxation rates several times lower than would have been expected based on prior models. Furthermore, spin-phonon interaction mitigation schemes such as phononic bandgap engineering [34, 35] will likely be ineffective in suppressing relaxation due to the short-wavelength, quasilocalized modes we find dominate. On the other hand, it may be possible to reduce relaxation rates by lowering the occupation number of the 167 meV phonon modes in a manner similar to optical cryocooling [36]. An improved microscopic picture of NV spin-phonon interactions is also important for understanding the behavior of the NV under DC strain, as both phonons and strain affect the NV primarily through nearest-neighbor carbon atoms [25, 37]. NV centers are already employed as sensors in high-strain environments, where preservation of coherence is critical [38–41]. In addition, NV spin-phonon relaxation is likely tunable by the intentional application of strain, an approach which has been shown to improve the coherence properties of the silicon-vacancy center in diamond [42]. Finally, the insights gained through our work can be generalized to other solid state defects with spin-1 electronic ground states and similar symmetries to the NV center, such as divacancy centers in silicon carbide [43, 44] or the boron vacancy center in diamond [45].

Conclusion.—We have presented measurements of the temperature dependence of the NV center’s single- and double-quantum relaxation rates in high-purity diamond samples from 9 to 474 K. Our \( ab \) initio calculation of the NV spin-phonon spectral function demonstrates that the dominant contributions to relaxation come from Raman transitions involving second-order interactions with phonons belonging to two distinct groups of quasilocalized modes. Accordingly, we have developed an analytical model of NV spin-phonon relaxation with just two effective phonon modes with characteristic energies of 68.2(17) and 167(12) meV. We calculated the limits imposed by spin-phonon relaxation on the coherence times of superpositions in the single- and double-quantum subspaces, accounting for the NV spin triplet dynamics over a wide range of temperatures in the phonon-limited regime for the first time. These results provide new upper bounds on NV center electronic spin coherence times that are critical for assessing the performance of experiments and the feasibility of proposed schemes in future quantum sensing and quantum communication research. In addition, the microscopic model of NV spin-phonon relaxation presented here suggests new possibilities for addressing or even exploiting spin-phonon interactions, and can likely be applied to other solid state spin-1 defects.

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**FIG. 4.** Temperature dependence of maximum relaxation-limited coherence times. Solid line shows \( T_{2,\text{max}} \) in the single-quantum subspace as a function of temperature according to Eq. 6, where \( \Omega \) and \( \gamma \) are calculated from Eqs. (4) and (5) for sample A. (See Supplemental Material for a version of this plot showing both samples and spin subspaces [16].) As in Fig. 2, the vertical gray line at 125 K demarcates the phonon-limited regime. The data points show the longest measured NV coherence times at various temperatures as reported in Refs. [29], [31], and [32]. Inset: Ratio of measured coherence times to corresponding relaxation limits.
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Supplemental Material for “Temperature-dependent phonon-induced relaxation of the nitrogen-vacancy spin triplet in diamond”

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EXPERIMENTAL DETAILS

Experiments were conducted using a homebuilt confocal microscope with dual support for low-temperature (9 K to ambient) and high-temperature (ambient to 474 K) operation modes (Fig. 1c of the main text). Switching between modes is accomplished with a flip-mounted mirror that routes the optical path between the low- and high-temperature setups. The low-temperature setup consists of an attocube attoDRY800 closed-cycle cryostat with a 0.82 NA cryogenic objective (attocube LT-APO/VISIR/0.82). The high-temperature setup consists of a homebuilt copper hot plate with a 0.55 NA long working distance (LWD) objective (Edmund Optics 59-879). The front of the LWD objective is actively cooled by air convection from a 12 V 50 × 50 × 10 mm case fan. In order to minimize vibrations, the case fan is mounted on a bench separate from the optical table and airflow is directed to the objective via a hose attached to the fan. An apertured aluminum plate is used to isolate the hot plate from the airflow. In our experience, an objective which has a shorter working distance or is not actively cooled can reach high temperatures and sustain permanent damage as a result. The temperature of the hot plate is stabilized by a custom proportional-integral-derivative (PID) feedback loop. In both operation modes, the diamond sample is thermally anchored to the cold finger/hot plate using conductive silver paint (Ted Pella Leitsilber). To accurately report the temperature of the diamond sample in high-temperature operation mode, we use the NV as a temperature sensor by inverting the temperature dependence of the zero field splitting reported in Ref. [1]. For low-temperature operation mode, we calibrated the cryostat’s integrated sample temperature sensor against an additional temperature sensor (Lakeshore CX-1050-SD-HT-1.4L-QT) mounted in the same manner as a diamond sample.

Optical polarization is achieved using a 1 ms pulse of approximately 1.5 mW of 532 nm light. The population in |0⟩ is readout optically by collecting fluorescence from the phonon sideband above 638 nm. Microwaves are delivered using a coplanar waveguide (CPW) mounted on top of the diamond sample. The CPW has an Ω-shaped loop along the signal trace which is shorted to the ground trace. The loop features an 1 mm diameter aperture in the center to allow for optical access to the sample underneath. It was manufactured by PCBWay and consists of a single 0.5 oz gold-plated copper layer on a 25 micron polyimide substrate. A coaxial connection is provided by a coplanar MMCX end-launch soldered onto pads at the end of the CPW.

Data from two different chemical-vapor-deposition grown samples is presented. Sample A, from Chenguang Machinery & Electric Equipment Company, displays an NV concentration of approximately 1 ppb. Measurements in this sample were performed on the ensemble of NVs within a single confocal volume, which we estimate contains about 30 (150) NVs of a given orientation for low-temperature (high-temperature) operation mode. Ensembles in high-temperature operation mode contain more NVs than ensembles in low-temperature operation mode due to the difference in NA between the low- and high-temperature mode objectives. Sample B, from Element Six, displays an inhomogeneous NV concentration with different areas exhibiting concentrations between 10−5 and 10−3 ppb. The higher-concentration regions are localized in irregularly-spaced planes, each approximately 5 microns thick. Measurements in sample B were conducted with single NVs isolated within the higher-concentration planes. The NV concentrations quoted in the main text are estimated by NV counting or by comparing the observed fluorescence rate to that of a single isolated NV. In both samples, measurements were conducted with NVs several microns below the diamond surface so as to avoid the effects of surface noise.
In several instances, we use a modified version of the standard relaxation rate experiment sequence described in prior works [2–4] in order to achieve more efficient measurements. For all measurements in sample A (the higher NV concentration sample), we use Knill composite $\pi$ pulses in place of standard $\pi$ pulses to drive spin state transitions. Knill pulses consist of five standard $\pi$ pulses with differing phases ($30^\circ$, $0^\circ$, $90^\circ$, $0^\circ$, $30^\circ$) applied in series. Knill pulses, like other composite $\pi$ pulses, are more robust against off-resonance errors than standard $\pi$ pulses and so help to mitigate the effect of inhomogeneous broadening within ensembles [5, 6]. For measurements in sample B (the lower NV concentration sample) below room temperature, we use spin-to-charge-conversion (SCC) readout in place of standard optical readout. In the standard readout scheme, NVs are excited with green illumination ($\sim 1.5$ mW) and the resultant spin-state dependent fluorescence is collected. Because the spin repolarizes during this process, readout is limited to roughly 300 ns during which $< 1$ photon is collected on average per experiment for single NVs. Each experiment must therefore be repeated $> 10^5$ times for sufficient averaging, leading to prohibitively long single-NV measurements at low temperatures. In contrast, in SCC readout a spin-state selective optical ionization pulse maps the NV spin state onto its charge state, which is then readout via fluorescence under weak ($\sim 10$ µW) yellow illumination [7]. The charge state is robust under the readout illumination, enabling long readouts ($\sim 10$ ms) during which tens of photons may be collected. For long experiments where the overhead of SCC readout is relatively small, SCC readout results in an enhanced measurement sensitivity that allows for the practical measurement of slow relaxation rates with single NVs. In order to verify that the modifications discussed in this paragraph (Knill pulses and SCC readout) do not introduce errors or artifacts into our measurements, we ran relaxation experiments at room temperature with standard and SCC readout as well as with standard $\pi$ pulses and Knill $\pi$ pulses and confirmed in each case that the modified sequences yield the same relaxation rates.

The assumption of a single-valued $\Omega$ to describe phonon-limited relaxation on both the $|0\rangle \leftrightarrow |-1\rangle$ and $|0\rangle \leftrightarrow |+1\rangle$ transitions has been verified empirically in previous work [4] and is consistent with all experimental data collected for this study.

**COMPARISON TO PRIOR MEASUREMENTS**

Several experimental studies have measured the temperature dependence of the single-quantum relaxation rate in bulk diamond samples [8–10]. In a recent study [12], Lin et al. report measurements of the temperature dependence of both the single- and double-quantum relaxation rates above room temperature. Measurements of the single- and double-quantum rates are reported in Refs. [11] and [4], but only at room temperature. The results from these prior studies are shown alongside the results presented in this work in Fig. S1. Our measurements of the single-quantum relaxation rate are consistent with the majority of prior results in low-density samples ($[\text{NV}] < 1$ ppm) to within approximately 10% [4, 9–11]. Interestingly, in the high-density samples ($[\text{NV}] \sim 10$ ppm) measured by Redman et al. and Jarmola et al. (sample S2), single-quantum relaxation rates were approximately 30% faster than the typical
TABLE S1. Sample-dependent constants from the fit of the model described by Eqs. (4) and (5) of the main text to the experimental data. The sample-dependent constant for $\Omega$ ($\gamma$) is denoted by $A_3$ ($B_3$).

|            | $A_3$ (Sample A) (s$^{-1}$) | $B_3$ (Sample A) (s$^{-1}$) | $A_3$ (Sample B) (s$^{-1}$) | $B_3$ (Sample B) (s$^{-1}$) |
|------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|            | 0.013(8)                    | 0.06(2)                     | 0.007(5)                    | 0.31(6)                     |

values seen in low-density samples [8, 10]. Jarmola proposed that this discrepancy is due to temperature-dependent cross-relaxation, an effect which is not captured by the sample-dependent constant terms in the model described by Eqs. (4) and (5) of the main text.

The single-quantum relaxation rates measured by Lin et al. in Ref. [12] are consistent with the rates measured by Redman and Jarmola in high-density samples, but surprisingly, the measurements in Ref. [12] were conducted using a low-density sample with a reported NV concentration of only 2 ppb. Lin’s observation of fast single-quantum relaxation in a low-density sample may indicate that the temperature-dependent cross-relaxation proposed by Jarmola involves a separate defect species; in this case NV concentration would not be a reliable indicator of the magnitude of cross-relaxation. In addition, Lin’s measurement of the double-quantum relaxation rate at room temperature for low-density samples is around 70% faster than the value established by previous work [4, 11] and replicated in this work. The temperature dependence of the double-quantum relaxation rate reported by Lin is also qualitatively different than that reported in this work; in Lin’s measurements, the double-quantum relaxation rate increases with temperature more slowly than the single-quantum relaxation, such that $\Omega > \gamma$ at $T > 450$ K. In contrast we find $\Omega < \gamma$ at all temperatures in the phonon-limited regime. It is difficult to reconcile this observation with our findings, even allowing for a temperature-dependent cross relaxation process involving a high concentration of dark defects in Lin’s sample. We conclude that the results of Ref. [12] are not entirely unprecedented, but are probably not applicable to the vast majority of samples studied by the NV community.

## SAMPLE-DEPENDENT BEHAVIOR AT LOW TEMPERATURES

At temperatures below 125 K, sample-dependent constants begin to make non-negligible contributions to the relaxation rates. The values of these constants as determined from the fit of the proposed model (Eqs. (4) and (5) in the main text) to the experimental data are shown in Table S1. We note that sample-dependent constants have been attributed to interactions between defects [10, 16]. Accordingly, it may be expected that samples with higher defect concentrations exhibit larger sample-dependent constants. While the samples studied for this work display this anticipated behavior for $\Omega$, we observe that the constant for $\gamma$ is around 5 times larger in sample B ($[\text{NV}] \approx 10^{-5}$ ppb)
than in sample A ([NV] ≈ 1 ppb). While a full investigation of this effect is out of scope for the present work, we suggest that the unexpectedly large constant for γ in sample B may be associated with a dark defect species present at higher levels in sample B than in sample A. Fig. S2 shows the effect of the sample-dependent constants on the relaxation-limited coherence times for samples A and B. We see that coherence times in sample A can in principle be over three times longer than in sample B at low temperatures as a result of sample-dependent relaxation.

**COMPARISON BETWEEN THE PROPOSED AND PRIOR ANALYTICAL MODELS**

In prior work [8, 10, 16], the analytical model used to describe the temperature dependence of the single-quantum relaxation rate Ω typically contains terms accounting for low-temperature behavior, an Orbach-like term which scales with the occupation number \( n = [\exp(\Delta/k_B T) - 1]^{-1} \) at a phonon energy \( \Delta \), and a \( T^5 \) term attributed to the effect of low-energy weakly coupled acoustic phonons. Here we develop an extended version of this prior model so that we can compare it to the model we propose in the main text (Eqs. (4) and (5)). As discussed in the main text, prior experimental work has tacitly assumed \( \gamma = 0 \) [8–10]. In these contexts the lifetime of \( |0\rangle \) is denoted \( T_1 \), which is equivalent to \( 1/3\Omega \). For clarity we denote this quantity \( T_1^{(0)} \) here. As a starting point, we consider the expression used by Jarmola et al. in Ref. [10]:

\[
\frac{1}{T_1^{(0)}} = A_1(S) + \frac{A_2}{\exp(\Delta/k_B T) - 1} + A_3 T^5.
\]  

(S1)

We note that the occupation number \( n \) is written in exponential form. As the Orbach-like term describes scattering of phonons at a specific energy \( \Delta \), the full temperature dependence of this term is \( n(n+1) \) [4]. Jarmola et al. simplify this by taking the low-temperature approximation \( n(n+1) \approx n \) for \( n \ll 1 \); we avoid this approximation here. With these considerations, we extend Eq. (S1) to describe both the single- and double-quantum relaxation rates \( \Omega \) and \( \gamma \):

\[
\Omega(T) = A_1 n(n + 1) + A_2 T^5 + A_3(S),
\]

(S2)

\[
\gamma(T) = B_1 n(n + 1) + B_2 T^5 + B_3(S).
\]

(S3)

Fits to the experimental data according to Eqs. (S2) and (S3) are nearly identical to those provided by the proposed model described by Eqs. (4) and (5) of the main text and shown in Fig. 2 of the main text. The normalized residuals for the two models are shown in Fig. S3. We see that both the proposed model (Eqs. (4) and (5) of the main text) and the prior model (Eqs. (S2) and (S3) of this document) provide excellent fits to the experimental data. As such, in the temperature range studied in this work it is not possible to say which model is more physically accurate from the fits alone. However,
FIG. S4. Ratio of $\gamma$ to $\Omega$ as a function of temperature in the phonon-limited regime. The lines are the ratios of the fits to the measured relaxation rates $\gamma$ and $\Omega$ according to the proposed model described by Eqs. (4) and (5) of the main text. As in Fig. 2 of the main text, the dotted (dashed) line includes sample-dependent constants for sample A (B). For both samples, the ratio passes near 2 at room temperature, as observed in Ref. [4].

The terms $T^5$ and $n(n + 1)$ exhibit dramatically different scalings at higher temperatures than those accessed in this or prior studies. Accordingly, it may be possible to demonstrate the breakdown of the prior model at temperatures of around 700 K, where the prior model predicts relaxation rates around 50% (20%) faster than the prior model for $\Omega$ ($\gamma$).

**RATIO OF $\gamma$ TO $\Omega$ AS A FUNCTION OF TEMPERATURE**

In Ref. [4], we observed that $\gamma \approx 2\Omega$. We previously speculated that this factor of 2 may be fundamental, implying that the ratio should be independent of temperature in the phonon-limited regime. Fig. S4 demonstrates that this is not the case, as the ratio decreases nearly linearly from approximately 2.5 at 150 K to approximately 1.5 at the highest temperatures accessed in this work. The decreasing ratio indicates that the single-quantum transition is more strongly coupled to the higher-energy effective phonon mode than is the double-quantum transition.

**AB INITIO CALCULATION OF THE SPIN-PHONON RELAXATION RATES**

We proceed with the ab initio calculation of the spin-phonon relaxation rates by first computing the spin-phonon matrix elements up to second order, then applying Fermi’s golden rule, and finally taking the continuum limit, converting sums over matrix elements into integrals over spectral functions. We note that we apply Fermi’s golden rule with the random phase approximation such that interference terms are dropped.

**Calculation of the spin-phonon matrix elements**

We calculate the spin-phonon matrix elements using plane wave supercell density functional theory (DFT). We apply the VASP implementation [17, 18] of the plane wave supercell DFT calculations with the projector augmented wave (PAW) method. The supercell consists of a 512-atom simple cubic diamond with a single negatively charged NV defect embedded in the center. We keep the optimized diamond lattice constant (3.567 Å) fixed during the geometry optimization procedure of the defective supercell. The forces acting on the atoms are lower than $10^{-4}$ eV/Å in the global energy minimum of the adiabatic potential energy surface (APES). We apply Γ-point sampling of the Brillouin-zone. We use a cutoff of 370 eV for the plane wave basis and a cutoff of 740 eV for charge augmentation in all calculations. The phonons together with the associated normal coordinates are calculated by building up the
Hessian matrix as the first numerical derivative of the forces acting on the atoms, where the atoms are moved by 0.015 Å in each direction and the resultant APES is fit to a parabola around the global energy minimum. The zero field splitting tensor (or D-tensor) is calculated within the PAW-method [19] as implemented by Martijn Marsman. In the global energy minimum of the APES, the D-constant is equal to (3/2)D_{zz} after diagonalization of the D-tensor. Spin-polarized Perdew-Burke-Ernzerhof (PBE) functionals [20] are employed in these procedures.

The spin-phonon matrix elements are then obtained by exploiting the dependence of the D-tensor on the normal coordinates:

$$\begin{equation}
\hat{D}(R) = \hat{D}(R = 0) + \sum_i \frac{\partial \hat{D}}{\partial R_i} \bigg|_{R=0} R_i + \frac{1}{2} \sum_{ij} \frac{\partial \hat{D}}{\partial R_i \partial R_j} \bigg|_{R=0} R_i R_j,
\end{equation}$$

where a homebuilt script is used to extract the coefficients in Eq. (S4). In order to evaluate the second-order derivatives, we consider only the diagonal terms which satisfy $i = j$ and distort the $C_{3v}$ symmetric atomic positions by all degenerate $e_x$, $e_y$ phonon modes of the supercell by $\sqrt{(\Delta \mathbf{R})^2} = 0.1 \text{Å}\sqrt{\text{a.m.u.}}$. The second-order spin-flipping matrix elements $V_{+0}^{ll}$ and $V_{+}^{ll}$ then determine the D-tensor according to the symmetry-adapted expression:

$$\begin{equation}
\hat{D}(R = 0) = \left( -\frac{1}{3}D \begin{array}{cc}
-\frac{1}{3}D \\
\frac{2}{3}D
\end{array} \right) + \text{linear terms} + \left( -\frac{1}{3} \begin{array}{cc}
-\frac{1}{3}D \\
\frac{2}{3}D
\end{array} \right) \sum_i 3V_{00}^{ll} R_i^2 + \\
+ \sum_l V_{+}^{ll} \left[ \begin{array}{cc}
1 \\
-1
\end{array} \right] (X_1^2 - Y_1^2) + \left[ \begin{array}{cc}
1 \\
-1
\end{array} \right] 2X_1Y_1 + \\
+ \sum_l \sqrt{2}V_{+0}^{ll} \left[ \begin{array}{cc}
1 \\
1
\end{array} \right] (X_1^2 - Y_1^2) + \left[ \begin{array}{cc}
1 \\
1
\end{array} \right] 2X_1Y_1 + ...
\end{equation}$$

where $R_i$, $X_i$ and $Y_i$ are the dimensionless coordinates (not normal coordinates) for the phonon mode at energy $\hbar \omega_i$ or $\hbar \omega_l$. We note that while the index $l$ only covers the e modes once, the index $i$ covers all $a_1$, $a_2$, $e_x$, $e_y$ modes and thus runs over the e modes twice. Therefore, we omit $e_z$'s degenerate partner $e_y$ modes from our calculations because their effect is the same. Eq. (S5) can be transformed into the spin-phonon interaction $\hat{V}$ by:

$$\hat{V} = \left( \hat{S} \hat{D} \hat{S} \right) = D(\hat{S}_z^2 - \frac{1}{3} \hat{S}(\hat{S} + 1)) + \text{linear terms} + \sum_i 3V_{00}^{ll}(\hat{S}_z^2 - \frac{1}{3} \hat{S}(\hat{S} + 1)) \hat{R}_i^2 + \\
+ \sum_l V_{+}^{ll} \left[ (\hat{S}_z^2 - \hat{S}_z^2)(\hat{X}_1^2 - \hat{Y}_1^2) + (\hat{S}_z \hat{S}_y + \hat{S}_y \hat{S}_z)(\hat{X}_1 \hat{Y}_1 + \hat{Y}_1 \hat{X}_1) \right] + \\
+ \sum_l \sqrt{2}V_{+0}^{ll} \left[ (\hat{S}_z \hat{S}_z + \hat{S}_z \hat{S}_z)(\hat{X}_1^2 - \hat{Y}_1^2) + (\hat{S}_y \hat{S}_z + \hat{S}_z \hat{S}_y)(\hat{X}_1 \hat{Y}_1 + \hat{Y}_1 \hat{X}_1) \right] + ...
$$

where $\hat{S} = (\hat{S}_x \hat{S}_y \hat{S}_z)$. We expand the dimensionless coordinates in terms of the phonon creation and annihilation operators: $\hat{R}_i = (b_i^0 + b_i)/\sqrt{2}$ and $\{\hat{X}_1, \hat{Y}_1\} = (b_{(X,Y)}^0 + b_{(X,Y)})/\sqrt{2}$.

**Relaxation due to first-order spin-phonon interactions**

The first-order analog of Eq. (2) in the main text describes the rate at which first-order interactions drive Raman transitions. According to Fermi’s golden rule taken to second order in perturbation theory,

$$\begin{equation}
\Gamma^{(1)}_{2(m,m')}(T) = \frac{2\pi}{h} \sum_{ll'} \delta(E_{m'} - E_m) + n_{l'} (n_{l'} + 1) \left| \frac{V_{m,m'}^{ll'} + V_{m',m'}^{ll}}{(E_{m'} - \hbar \omega_l) - E_m} \right|^2 \delta(\Delta E_{-}) + n_{l'} (n_{l'} + 1) \left| \frac{V_{m,m'}^{ll'} + V_{m',m'}^{ll}}{(E_{m'} + \hbar \omega_l) - E_m} \right|^2 \delta(\Delta E_{+}),
\end{equation}$$
where the $V_{m,m'}^l$ are the first-order spin-phonon coupling coefficients from the first-order spin-phonon interaction $\hat{V}^{(1)} = \sum_{lm} V_{lm}^l(a_l + a_l^\dagger)$. As in the main text, $\Delta E_k = E_{m'} - (\hbar \omega_l - \hbar \omega_l') - E_{m_s}$ is the energy difference between the final and initial states of the composite system. Making the approximation that the energy of the NV is small in comparison to the typical phonon energies, in validation of the argument presented in the main text, the $ab$ initio estimate the first-order interaction contributions to relaxation by comparing the magnitude of the spectral function elements, but rather depend on products of the first-order matrix elements according to Eq. S9. Nevertheless, we can interations, Raman transitions involving first-order interactions are not directly related to the first-order matrix lines) for a single NV center in a 512 atom supercell. Like in Fig. 3 of the main text, we plot the coupling coefficients and spectral function has the same double-peaked lineshape as the second-order spectral function. The spectral function is much smaller than the energies of the associated phonons, indicating that first-order interactions make negligible contributions to relaxation. As in Fig. 3 of the main text, the gray lines and confidence intervals mark the locations of the effective phonon smaller than the energies of the associated phonons, indicating that first-order interactions make negligible contributions to.

\[
\Gamma_{2(m,m')}^{(1)}(T) = \frac{4\pi}{\hbar} \sum_{ll'} \sum_{mm''} n_l (n_{l'} + 1) \left| \frac{V_{lm}^l V_{l'm'}^{l'}}{\omega_l} \right|^2 \delta(\omega_{l'} - \omega_l). \tag{S8}
\]

In the continuum limit we replace the coupling coefficients with the first-order spectral function $F_{m,m'}^{(1)}(\omega) = \sum_l |V_{lm}^l|^2 \delta(\omega - \omega_l)$ and obtain

\[
\Gamma_{2(m,m')}^{(1)}(T) = \frac{4\pi}{\hbar} \sum_{m''} \int_0^\infty d(\omega') n(\omega') \left| \frac{F_{m,m''}^{(1)}(\omega) F_{m''m'}^{(1)}(\omega)}{\omega^2} \right|. \tag{S9}
\]

We estimate the first-order spectral function for a macroscopic diamond by convolving the first-order coupling coefficients with a Gaussian of variance $\sigma^2 = 7.5$ meV:

\[
F_{m,m'}^{(1)}(\omega) = \int d(\omega') \sum_l |V_{lm}^l|^2 \delta(\omega' - \omega_l) \times \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{(\omega' - \omega_l)^2}{2\sigma^2}\right). \tag{S10}
\]

The $ab$ initio first-order coupling coefficients and spectral function are displayed in Fig. S5. Unlike for second-order interactions, Raman transitions involving first-order interactions are not directly related to the first-order matrix elements, but rather depend on products of the first-order matrix elements according to Eq. S9. Nevertheless, we can estimate the first-order interaction contributions to relaxation by comparing the magnitude of the spectral function to the typical phonon energies. In validation of the argument presented in the main text, the $ab$ initio first-order matrix elements are on the order of MHz, much smaller than the energies of the associated phonons ($\sim 10$ THz). We calculate that first-order interactions drive relaxation at rates several orders of magnitude slower than second-order interactions.

**Relaxation due to second-order spin-phonon interactions**

From Fermi’s golden rule taken to first order in perturbation theory, the second-order interaction $\hat{V}^{(2)} = \sum_{ll'm'm'} V_{ll'm'm'}^{ll'} (a_l^\dagger a_l)(a_{l'}^\dagger + a_{l'})$ from Eq. (S6) drives Raman scattering at the rate shown in Eq. (2) of the
main text, which we reproduce here:

$$\Gamma^{(2)}_{1(m_s, m_s')} (T) = \frac{2\pi}{\hbar} \sum_{ll'} |V^l_{m_s m_s'}|^2 \left[ n_l (n_{l'} + 1) \delta (\Delta E_-) \right],$$

(S11)

Again assuming that the NV energies are small in comparison to the phonon energies,

$$\Gamma^{(2)}_{1(m_s, m_s')} (T) = 4\pi \frac{\hbar}{\Delta} \sum_{ll'} n_l (n_{l'} + 1) \left| V^l_{m_s m_s'} \right|^2 \delta (h \omega_l - h \omega_{l'}).$$

(S12)

We transform Eq. (S12) into its integral form:

$$\Gamma^{(2)}_{1(m_s, m_s')} (T) = \frac{4\pi}{\hbar} \int_0^\infty \int_0^\infty d(h \omega) d(h \omega') n(\omega) (n(\omega) + 1) F^{(2)}_{m_s m_s'} (h \omega, h \omega') \delta (h \omega_l - h \omega_{l'}),$$

(S13)

by introducing the second-order spectral function $F^{(2)}_{m_s m_s'} (h \omega, h \omega') = \sum_{ll'} |V^l_{m_s m_s'}|^2 \delta (h \omega_l - h \omega_{l'}).$ The $\delta (h \omega_l - h \omega_{l'})$ delta function in Eq. (S13) can be integrated out:

$$\Gamma^{(2)}_{1(m_s, m_s')} (T) = \frac{4\pi}{\hbar} \int_0^\infty d(h \omega) n(\omega) (n(\omega) + 1) F^{(2)}_{m_s m_s'} (h \omega, h \omega').$$

(S14)

Following Eq. S10, we estimate the second-order spectral function for a macroscopic diamond by convolving the second-order coupling coefficients with a Gaussian of variance $\sigma^2 = 7.5$ meV:

$$\sqrt{F^{(2)}_{m_s m_s'} (h \omega, h \omega')} = \int d(h \omega') \sum_l |V^l_{m_s m_s'}| \delta (h \omega_l - h \omega_{l'}) \times \frac{1}{\sigma \sqrt{2\pi}} \exp \left(-\frac{(h \omega - h \omega_l)^2}{2\sigma^2} \right).$$

(S15)

We plot the square root of $ab$ \textit{initio} spectral function in Fig. 3. of the main text. Ignoring degeneracies, we note that the $h \omega_l = h \omega_{l'}$ constraint also enforces that $l = l'$ and so we only consider the $V^l_{m_s m_s'}$ diagonal matrix elements in our $ab$ \textit{initio} calculation.

Fig. S6a compares the relaxation rates predicted by the $ab$ \textit{initio} theory in comparison to the fit of the analytical model to the experimental data. We obtain the predicted relaxation rates by evaluating Eq. (3) of the main text.
FIG. S7. Semi-log version of Fig. 2 from the main text showing the full temperature range over which experiments were conducted for this work. The rates predicted by the \textit{ab initio} calculation are not shown.

using the calculated second-order spin-phonon spectral function for the single- and double-quantum transitions shown in Fig. 3 of the main text. The \textit{ab initio} theory achieves near quantitative agreement with experiment and captures several important features (Fig. S6b). In particular, we observe that the theory reproduces the experimental finding that $\gamma > \Omega$. The theory curves also closely follow the lineshapes of the experimental curves, as evidenced by the flat ratios between the \textit{ab initio} and model rates in the phonon-limited regime.

**COMPLETE SET OF EXPERIMENTALLY MEASURED RATES**

Fig. S7 and table S2 display the complete set of experimentally measured rates collected for this work. In the table, NVs are indexed first by sample and then numerically to distinguish single NVs in sample B.
| NV | $T$ (K) | $\Omega$ (s$^{-1}$) | $\gamma$ (s$^{-1}$) | NV | $T$ (K) | $\Omega$ (s$^{-1}$) | $\gamma$ (s$^{-1}$) |
|----|---------|---------------------|---------------------|----|---------|---------------------|---------------------|
| NVA | 8.9 | $1.7(9) \times 10^{-2}$ | $5(3) \times 10^{-2}$ | NVA | 390.3 | $1.65(7) \times 10^{2}$ | $2.6(2) \times 10^{2}$ |
| NVA | 50.0 | $2(2) \times 10^{-2}$ | $9(6) \times 10^{-2}$ | NVA | 401.6 | $1.79(7) \times 10^{2}$ | $3.5(2) \times 10^{2}$ |
| NVA | 84.6 | $4(2) \times 10^{-2}$ | $5(2) \times 10^{-1}$ | NVA | 415.6 | $2.13(10) \times 10^{2}$ | $3.7(3) \times 10^{2}$ |
| NVA | 124.1 | 1.00(9) | 3.4(4) | NVA | 427.1 | $2.43(10) \times 10^{2}$ | $3.6(2) \times 10^{2}$ |
| NVA | 148.4 | 2.64(16) | 7.0(6) | NVA | 440.1 | $2.54(11) \times 10^{2}$ | $4.1(3) \times 10^{2}$ |
| NVA | 158.6 | 4.0(3) | $1.03(8) \times 10^{1}$ | NVA | 454.0 | $2.62(11) \times 10^{2}$ | $4.3(3) \times 10^{2}$ |
| NVA | 160.9 | 4.0(3) | $1.21(9) \times 10^{1}$ | NVA | 465.5 | $3.04(13) \times 10^{2}$ | $5.2(3) \times 10^{2}$ |
| NVA | 172.9 | 6.2(2) | $1.66(8) \times 10^{1}$ | NVA | 471.4 | $3.37(15) \times 10^{2}$ | $5.2(3) \times 10^{2}$ |
| NVA | 184.9 | 8.3(4) | $2.09(13) \times 10^{1}$ | NVA | 497.5 | $1.33(3) \times 10^{3}$ | $3.0(4) \times 10^{3}$ |
| NVA | 196.9 | $1.14(5) \times 10^{1}$ | $2.32(16) \times 10^{1}$ | NVB2 | 244.7 | $2.7(2) \times 10^{1}$ | $7.3(7) \times 10^{1}$ |
| NVA | 208.5 | $1.45(7) \times 10^{1}$ | $3.9(2) \times 10^{1}$ | NVB1 | 295.0 | $5(1) \times 10^{1}$ | $1.2(4) \times 10^{2}$ |
| NVA | 221.4 | $1.91(10) \times 10^{1}$ | $5.2(3) \times 10^{1}$ | NVB5 | 295.0 | $5.1(5) \times 10^{1}$ | $1.31(15) \times 10^{2}$ |
| NVA | 233.5 | $2.23(10) \times 10^{1}$ | $5.7(4) \times 10^{1}$ | NVB4 | 295.0 | $6.5(5) \times 10^{1}$ | $1.23(13) \times 10^{2}$ |
| NVA | 244.7 | $2.85(13) \times 10^{1}$ | $7.2(4) \times 10^{1}$ | NVB5 | 344.3 | $1.06(9) \times 10^{2}$ | $2.2(2) \times 10^{2}$ |
| NVA | 256.4 | $3.54(17) \times 10^{1}$ | $7.9(5) \times 10^{1}$ | NVB4 | 344.9 | $8(1) \times 10^{1}$ | $1.9(4) \times 10^{2}$ |
| NVA | 268.8 | $4.5(2) \times 10^{1}$ | $9.1(7) \times 10^{1}$ | NVB5 | 393.0 | $1.60(13) \times 10^{2}$ | $3.4(4) \times 10^{2}$ |
| NVA | 281.4 | $5.4(3) \times 10^{1}$ | $1.05(8) \times 10^{2}$ | NVB5 | 393.6 | $1.77(16) \times 10^{2}$ | $2.9(4) \times 10^{2}$ |
| NVA | 295.0 | $6.0(3) \times 10^{1}$ | $1.28(7) \times 10^{2}$ | NVB4 | 441.1 | $2.7(3) \times 10^{2}$ | $5.2(8) \times 10^{2}$ |
| NVA | 301.5 | $6.0(2) \times 10^{1}$ | $1.32(7) \times 10^{2}$ | NVB5 | 473.3 | $3.2(3) \times 10^{2}$ | $5.8(7) \times 10^{2}$ |
| NVA | 308.1 | $7.3(3) \times 10^{1}$ | $1.50(10) \times 10^{2}$ | NVB5 | 473.3 | $3.5(3) \times 10^{2}$ | $5.0(7) \times 10^{2}$ |
| NVA | 323.8 | $8.7(5) \times 10^{1}$ | $1.30(12) \times 10^{2}$ | NVB4 | 473.5 | $3.9(3) \times 10^{2}$ | $5.9(6) \times 10^{2}$ |
| NVA | 328.3 | $7.8(5) \times 10^{1}$ | $1.57(10) \times 10^{2}$ | NVB4 | 473.5 | $3.9(3) \times 10^{2}$ | $5.9(6) \times 10^{2}$ |
| NVA | 337.6 | $1.01(5) \times 10^{2}$ | $1.95(13) \times 10^{2}$ | NVB4 | 473.5 | $3.9(3) \times 10^{2}$ | $5.9(6) \times 10^{2}$ |
| NVA | 353.7 | $1.14(5) \times 10^{2}$ | $2.27(15) \times 10^{2}$ | NVB4 | 473.5 | $3.9(3) \times 10^{2}$ | $5.9(6) \times 10^{2}$ |
| NVA | 368.7 | $1.32(6) \times 10^{2}$ | $2.51(17) \times 10^{2}$ | NVB4 | 473.5 | $3.9(3) \times 10^{2}$ | $5.9(6) \times 10^{2}$ |
| NVA | 380.4 | $1.38(6) \times 10^{2}$ | $2.8(2) \times 10^{2}$ | NVB4 | 473.5 | $3.9(3) \times 10^{2}$ | $5.9(6) \times 10^{2}$ |

**TABLE S2.** Complete set of experimentally measured rates collected for this work.
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