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Vibrational quenching of the electronic ground state in ThO in cold collisions with ^{3}He

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We measure the ratio γ of the momentum transfer–to–vibrational quenching cross section for molecular thorium monoxide (ThO) $[X(^1\Sigma^+), v = 1, J = 0]$ in collisions with atomic helium between 800 mK and 2.4 K. We find $\gamma \sim 10^4$. We also observe indirect evidence for ThO-He van der Waals complex formation, which has been predicted by theory [Tscherbul, Sayfutyarova, Buchachenko, and Dalgarno, J. Chem. Phys. **134**, 144301 (2011)], and in conjunction, we determine the three-body recombination rate constant at 2.4 K, $\Gamma_3 = 8 \pm 2 \times 10^{-33}$ cm^6 s^{-1}.

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I. INTRODUCTION

Cold and ultracold molecules have the potential to impact the fields of precision measurement [1], quantum simulation [2], and cold controlled chemistry [3]. Recent advances in the production of ultracold KRb from laser-cooled atoms have led to the demonstration of quantum-state-dependent chemical reactions [4] and dipolar interactions [5]. Cold molecular beams with temperatures of a few kelvins have significantly improved the sensitivity of electron EDM searches [6,7] and enhanced the differentiation of chiral molecules [8].

The full utility of molecules, will be achieved in these relatively new physical systems by exploiting their additional degrees of freedom, i.e., rotational and vibrational states. For example, rotational states could be efficiently coupled to solid-state quantum devices via microwave radiation [9], and vibrational states could be used for sensitive tests of variation in the proton-to-electron mass ratio [10] and to encode quantum information [11].

Compared to atomic collisions [12], molecular collisions are poorly understood, although recent progress has been impressive [13–15]. Molecule-atom collisions remain a benchmark platform for understanding these new collisional systems, particularly in the case of rotational and vibrational state-changing processes. Photo association [16], Stark deceleration [17,18], and buffer-gas cooling [19] are the main experimental tools for studying such collisions. Photo association enables study at ultracold temperatures but is currently limited to molecules formed by alkali and alkaline earth atoms [16], Stark deceleration allows tunable collisional energies with ~1 K resolution but so far can probe only collisions with energies above ~30 K [19], and buffer-gas cooling provides access to ~0.5 K.

There are three temperature ranges for atomic and molecular collisions: low (Wigner regime), intermediate [van der Waals (vdW) regime], and high. These ranges are characterized by the relative size of the depth of the interaction potential and the typical collisional energy. At intermediate temperatures, comparable to the energy of the vdW interaction, effects such as shape and Feshbach resonances can lead to an increased quenching rate at lower temperatures [20]. At high temperatures, resonant effects are averaged out over the range of collisional energies. At lower temperatures, collision energies are insufficient to overcome energy barriers in the medium range, resulting in collisional properties depending only on the long-range part of the interaction potential and possibly the positions of bound states in the potential. Study below the vdW temperature (~10 K) can provide useful constraints on potential energy surfaces.

In this paper, we focus on vibrational quenching collisions between molecular thorium monoxide (ThO) and atomic helium (^{3}He) in the intermediate vdW regime. We determine that vibrational states relax more rapidly than vdW molecule formation. Our work extends the experimental study of vibrational quenching to include closed-shell molecules.

II. EXPERIMENTAL SETUP

At the heart of our experimental approach is the production of a cold ThO molecular gas in the presence of cold ^{3}He. We create cold ThO molecules using the technique of buffer-gas cooling [21]. Our apparatus is similar to that of Ref. [22]. Using a dilution refrigerator, we cool a copper cell to a temperature of 0.8–4 K. We ablate a ThO_2 ceramic target with a YAG laser pulse of a few millijoules to produce ThO molecules, which then collide with ^{3}He and thermalize their translational motion to the cell's temperature. To calibrate the density of ^{3}He, we simultaneously ablate chromium (Cr) metal to produce a gas of cold atomic Cr and measure the Cr diffusion rate in the buffer gas. Cr is detected via laser absorption spectroscopy using the $3d^5 3d^5(6S)\,4s\,(a\,^7S_3) \rightarrow 3d^5\,(6S)\,4p\,(z\,^7P_4)$ transition at 426 nm. To extract the ^{3}He density, we adapt the value of $\sigma_d = 1.1 \times 10^{-14}$ cm^2 for the Cr-^{3}He diffusion cross section [23]. σ_d can potentially vary with temperature, as observed in other atomic [24,25] and molecular [26] systems. In order to be conservative, we simply take these shifts seen in other experiments and use our known temperature uncertainty, resulting as a source of systematic error in the measured rates at the tens of percent level.

III. VAN DER WAALS MOLECULES

It has been predicted theoretically [27] that ThO forms ThO-He vdW molecules in the presence of dense helium gas below 10 K. Noble-gas vdW molecules have been studied

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in a wide range of experiments, from supersonic jets [28] to bulk liquid helium [29] to buffer-gas cells [30]. In our setup, vdW molecules can be formed via a three-body recombination process,

$$\mathrm{ThO} + \mathrm{He} + \mathrm{He} \underset{\Gamma_2}{\overset{\Gamma_3}{\rightleftharpoons}} \mathrm{ThO-He} + \mathrm{He}, \tag{1}$$

where Γ_2 and Γ_3 are rate coefficients for two-body dissociation and three-body recombination, respectively. Suppose we begin our experiment by injecting free ThO molecules into a gas of helium. The vdW molecule formation dynamics of the system can be described by

$$\frac{d[\mathrm{ThO}]}{dt} = -\frac{\Gamma_D}{[\mathrm{He}]}[\mathrm{ThO}] + \Gamma_2[\mathrm{He}][\mathrm{ThO-He}] - \Gamma_3[\mathrm{He}]^2[\mathrm{ThO}], \tag{2}$$

$$\frac{d[\mathrm{ThO-He}]}{dt} = -\frac{\Gamma_D}{[\mathrm{He}]}[\mathrm{ThO-He}] - \Gamma_2[\mathrm{He}][\mathrm{ThO-He}] + \Gamma_3[\mathrm{He}]^2[\mathrm{ThO}], \tag{3}$$

where Γ_D is the diffusive rate constant. Note that the diffusive decay rate is inversely proportional to the helium density.

The density of free ThO molecules evolves as the sum of two exponential decays (Fig. 1), with time constants given by

$$\tau_s = \left(\frac{\Gamma_D}{[\mathrm{He}]} + \Gamma_2[\mathrm{He}] + \Gamma_3[\mathrm{He}]^2\right)^{-1}, \tag{4}$$

$$\tau_l = \frac{[\mathrm{He}]}{\Gamma_D}. \tag{5}$$

Here τ_s and τ_l represent time constants for the return to thermal equilibrium between ThO and ThO-He and for diffusive decay, respectively. We probe the ground X $(v = 0)$ state of free ThO molecules via absorption on the X $(v = 0) \rightarrow$ C $(v = 0)$ R(0) transition at 690 nm (Fig. 2). By repeating the experiment at various helium densities (Fig. 3), we extract these time constants. The linear dependence of τ_l on the helium density confirms our interpretation of it as the diffusive decay time constant. From these data, we determine the ratio between values of σ_d for ThO-^{3}He and Cr-^{3}He collisions to be $\sim$2 at 2.4 K. By fitting the τ_s data to Eq. (4) (Fig. 3), we also determine the three-body recombination rate constant to be $\Gamma_3 = 8 \pm 2 \times 10^{-33}$ cm^6 s^{-1}, which can be compared to the value of 10^{-31} cm^6 s^{-1} measured for the Ag-^{3}He system [30]. The error bar is statistical.

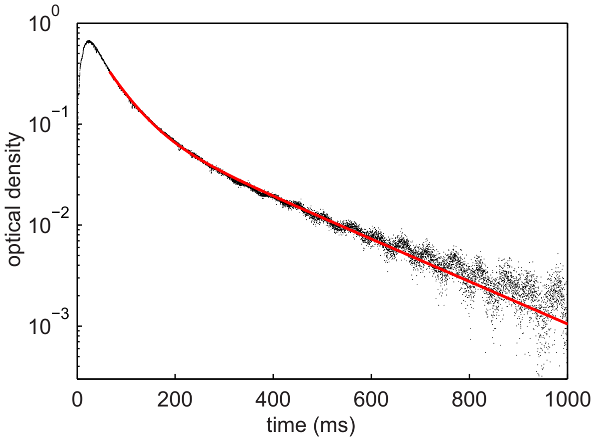

FIG. 1. (Color online) Optical density (OD) decay of ThO in its X $(v = 0, J = 0)$ state at a high helium density ($n_{\mathrm{He}} = 3 \times 10^{16}$ cm^{-3}) and 2.4 K (single shot). The solid (red) line is fit to a sum of two exponentials corresponding to ThO loss to diffusion and to vdW molecule formation. We verify that both diffusion modes and temperature stabilize within the first 50 ms by observing decay of atomic chromium produced simultaneously (not shown). The apparent oscillation visible at late times (small OD) is caused by mechanical vibration of the apparatus, and it has no significant effect on the early-time (large-OD) fitted lifetime.

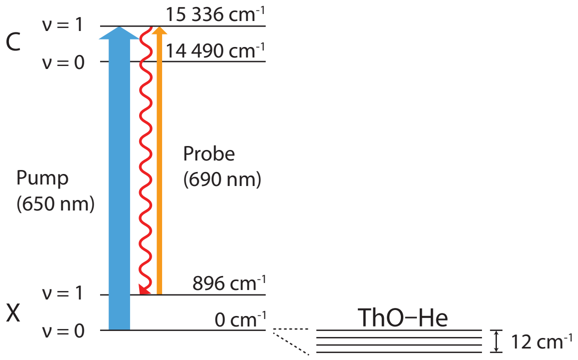

FIG. 2. (Color online) Relevant energy levels of the ThO molecule. Letters refer to the electronic states, X $(^1\Sigma^+)$ and C (77% $^1\Pi$, 20% $^3\Pi$), respectively. All measurements were performed in the ground rotational levels, $J = 0$ for the X state and $J = 1$ for the C state. Optical pumping via the X $(v = 0) \rightarrow$ C $(v = 1)$ R(0) transition at 650 nm is used to transfer the population to the X $(v = 1)$ state, which is probed using the X $(v = 1) \rightarrow$ C $(v = 1)$ R(0) transition at 690 nm. The relative scale of ThO-He bound-state energies is also shown.

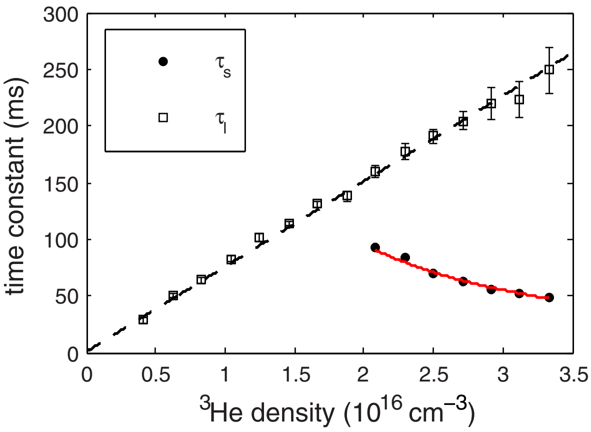

FIG. 3. (Color online) Fits to early- and late-time decay-time constants τ_s and τ_l in Eq. (4) and Eq. (5) at various helium densities at 2.4 K. Open squares (filled circles) denote fitted values for τ_l (τ_s). The dashed black line and solid (red) line are fits to Eq. (5) and Eq. (4), respectively, where the diffusive rate constants in Eq. (2) are extracted.

Although we extract a value for Γ_2 from the fit, its interpretation is not straightforward. In Eq. (2) and Eq. (3), we simplify our system to possess only one ThO-He vdW bound state. Under this simplification, $\Gamma_2 = ce^{-kT/E_b}$, for some constant c and binding energy E_b, both of which can be determined by repeating the experiment at a different temperature. However, from Ref. [27], we estimate that there are about 30 ThO-^{3}He vdW bound states. (No specific prediction was made in Ref. [27] for this system.) Similar binding energies are predicted for ^{3}He and ^{4}He vdW binding in other atomic and molecular systems [30]. As a result, the dissociation rate constant is a sum over all bound states,

$$\Gamma_2 = \sum_i c_i f_i e^{-kT/E_{b,i}}, \tag{6}$$

where f_i is the fractional occupation for bound state i. Therefore, the measured value of Γ_2 is a thermally averaged rate convolved with vdW molecule formation dynamics and vdW bound-state-changing collisions. The highest temperature at which we observe a decay of the form predicted by Eq. (4) and Eq. (5) is 4 K, and thus we conclude that there exist vdW bound states with binding energy $E_b/k_B > 4$ K, where k_B is the Boltzmann constant.

IV. VIBRATIONAL QUENCHING

To measure vibrational quenching in ThO molecules, we use an optical pump-and-probe technique. We transfer the molecule population from the absolute ground state to the first vibrationally excited state via the X $(v = 0) \rightarrow$ C $(v = 1)$ R(0) transition at 650 nm. We probe the X $(v = 1)$ state using the X $(v = 0) \rightarrow$ C $(v = 1)$ R(0) transition at 690 nm (Fig. 2). All measurements are performed in the ground rotational levels, $J = 0$ for the X state and $J = 1$ for the C state.

As shown in Fig. 4, laser ablation of the solid ThO$_2$ target produces a significant population in the X $(v = 1)$ state. However, this population fluctuates strongly between ablation shots in both magnitude and duration, presumably due to the different initial populations of higher-lying states, which then decay to the $v = 0$ state through the $v = 1$ state. Hence, we cannot use the initial-state population to study the dynamic of vibrational quenching.

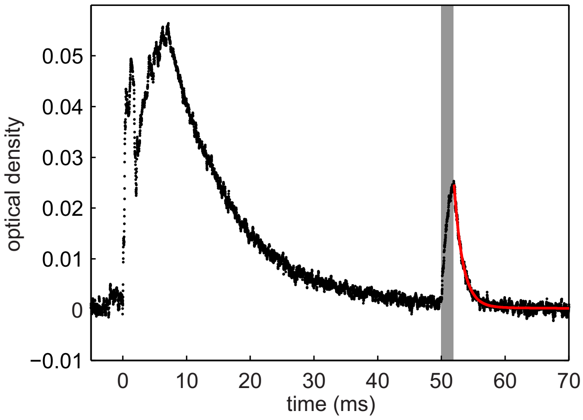

FIG. 4. (Color online) Optical density (OD) of ThO in its X $(v = 1, J = 0)$ state at 1.2 K (single shot). The initial OD, produced by molecule production via laser ablation, varies in both magnitude and duration and therefore it is unsuitable for the study of vibrational quenching. Instead, at 50 ms, a short optical pumping pulse [shaded (gray) area] transfers the population from the X $(v = 0, J = 0)$ state. This method removes noise from shot-to-shot fluctuation. The solid (red) line at the right is a fit to a single-exponential decay.

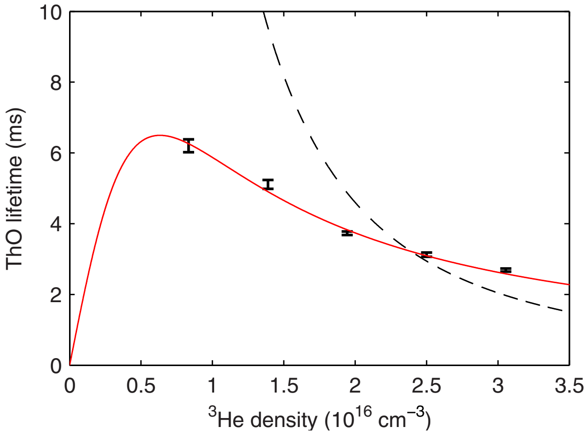

FIG. 5. (Color online) Observed vibrational quenching of the X $(v = 1, J = 0)$ state of ThO at 1.2 K. Error bars are statistical uncertainties. The ^{3}He density is determined from the diffusive decay of Cr produced simultaneously [23]. The solid (red) line is a combined diffusion, two-body, and three-body fit to the data [Eq. (7)]. The dashed black line is a three-body fit. The effect of diffusion is insignificant for $n_{\mathrm{He}} \gtrsim 1.2 \times 10^{16}$ cm^{-3}.

Instead, we wait for the initial population to decay and then apply an optical pumping pulse 50 ms after ablation to transfer the population from the $v = 0$ to the $v = 1$ state. We fit a single-exponential decay to the $v = 1$ population after optical pumping and repeat the experiment over a range of helium densities. We obtain the same results when the optical pumping pulse is instead applied 10 ms later and, therefore, conclude that the contribution to the fitted decay from the initial population is insignificant.

The measured lifetime of the ThO X $(v = 1)$ state $\tau_{v=1}$ at various helium densities n_{He} is shown in Fig. 5. There are three mechanisms for decay from this state: diffusion ($\tau_d \propto n_{\mathrm{He}}$), vibrational quenching ($\tau_q \propto n_{\mathrm{He}}^{-1}$), and vdW molecule formation ($\tau_3 \propto n_{\mathrm{He}}^{-2}$):

$$\tau_{v=1} = \left(\frac{1}{\tau_d} + \frac{1}{\tau_q} + \frac{1}{\tau_3}\right)^{-1} \tag{7}$$

$$= \left(\frac{1}{\tau_d} + C\frac{\tau_d}{\gamma} + \frac{1}{\tau_3}\right)^{-1} \tag{8}$$

$$= \left(\frac{A}{n_{\mathrm{He}}} + \frac{C}{A}\frac{n_{\mathrm{He}}}{\gamma} + Bn_{\mathrm{He}}^2\right)^{-1}, \tag{9}$$

$$C = \frac{3\pi}{32}\bar{v}^2\left(\frac{j_{01}^2}{R^2} + \frac{\pi^2}{L^2}\right), \tag{10}$$

where A is a fitting parameter describing diffusion that includes the ratio of ThO-He and Cr-He momentum transfer cross sections; B and γ, the ratio of the momentum transfer to the vibrational quenching cross section, are fitting parameters;

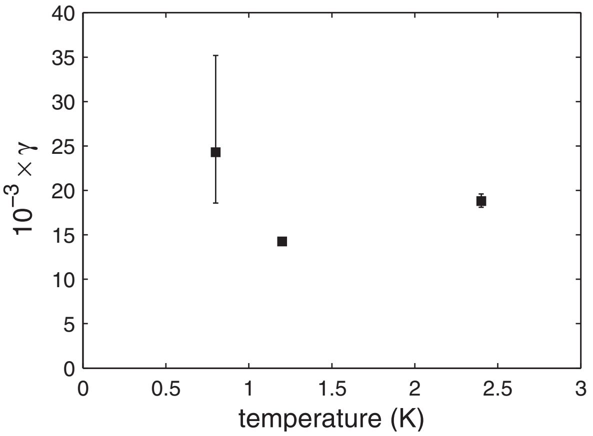

FIG. 6. Collisional quenching of the first vibrationally excited state of ThO in collisions with ^{3}He. Shown is the ratio γ of the momentum transfer to the vibrational quenching cross section for the X ($^1\Sigma^+$), $v = 1$, $J = 0$ state versus the temperature.

$\bar{v}$ is the mean thermal speed; j_{01} is the first zero of the Bessel function J_0; and R and L are the cell's radius and length, respectively [23]. We assume an identical momentum transfer cross section for both ThO ($v = 0$)–^{3}He and ThO ($v = 1$)–^{3}He. In deriving Eq. (8) from Eq. (7), we note the fact that the vibrational quenching rate τ_q^{-1} is proportional to the helium density n_{He}, which in turn is proportional to the diffusion time τ_d. At $n_{\mathrm{He}} \gtrsim 1.2 \times 10^{16}$ cm^{-3}, the effect of diffusion is insignificant. No theoretical prediction has been made for vdW molecule formation in the X ($v = 1$) state. The combined fit indicates that three-body recombination accounts for less than 25% of the observed $v = 1$ decay.

We measure vibrational quenching at three temperatures by fitting lifetime measurements to Eq. (7) (Fig. 6). The relatively large error bar for the 800 mK measurement is caused by the low ThO density, probably due to the lack of free ground-state molecules at lower temperatures.

Since mixing of rotational states in collisions is expected to be more rapid than vibrational quenching [27], our results are averaged over the first few rotational states. Compared to the reported vibrational quenching rates in CaH-He [23] and CO-He [31], our value for ThO-^{3}He is 2–4 orders of magnitude faster. One possible reason is that more shape resonances and Feshbach resonances are supported by a stronger vdW interaction between ThO and ^{3}He. The results remain to be explained by detailed theoretical calculations.

V. CONCLUSION

We obtain indirect evidence for vdW bound states between ThO and ^{3}He by observing loss of free ThO at a high helium density and low temperature. We determine the three-body recombination rate constant to be $\Gamma_3 = 8 \pm 2 \times 10^{-33}$ cm^6 s^{-1} at 2.4 K.

We also determine the ratio γ of the momentum transfer to the vibrational quenching cross section of the X ($^1\Sigma^+$), $v = 1$, $J = 0$ state. We find $\gamma \sim 10^4$, which suggests that sympathetic cooling of the vibrational modes can be slow. On the other hand, the long collisional lifetime of the $v = 1$ state may also lead to a wide range of applications such as vibrational qubits [11] when other cooling methods are deployed.

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