Isotope effects in collisional VT relaxation of molecular hydrogen

R. J. Bieniek

Physics Department, University of Missouri-Rolla, Rolla, MO 65409-0640

`bieniek@umr.edu`

ABSTRACT

A simple exponential-potential model of molecular collisions leads to a two-parameter analytic expression for rates of collisionally induced vibrational-translation (VT) energy exchange that has been shown to be accurate over variations of orders of magnitude as a function of temperature in a variety of systems. This includes excellent agreement with reported experimental and theoretical results for the fundamental self-relaxation rate of molecular hydrogen $H_2(v = 1) + H_2 \rightarrow H_2(v = 0) + H_2$. The analytic rate successfully follows the five-orders-of-magnitude change in experimental values for the temperature range 50-2000 K. This approach is now applied to isotope effects in the vibrational relaxation rates of excited HD and D_2 in collision with H_2: $HD(v = 1) + H_2 \rightarrow HD(v = 0) + H_2$ and $D_2(v = 1) + H_2 \rightarrow D_2(v = 0) + H_2$. The simplicity of the analytic expression for the thermal rate lends itself to convenient application in modeling the evolving vibrational populations of molecular hydrogen in shocked astrophysical environments.

1. VT transitions in shocked environments

In many astrophysical environments, shock fronts can significantly disturb the thermodynamic equilibrium between the kinetic and vibrational motion of quiescent molecular species present (as in cold molecular clouds). Although kinetic energies can rise rapidly in response to the shock, vibrational populations are slower to respond, producing non-LTE situations. Molecular collisions drive the vibrational populations to become equilibrated with thermal kinetic energy by inducing energy exchange between vibrational and translational (VT) forms. The VT rate will determine the evolution of relative populations of vibrational levels in such disturbed environments where the vibrational and translational temperatures are not equilibrated. This will affect an astrophysical systems spectroscopy, energetics, reactions, and radiative signatures.

The evolution of vibrational populations can be calculated if state-to-state rates for vibrational-rotational transitions are available for the species desired. However, these are often hard to come by. Yet, much modeling and analysis can be done by lumping all the rotational states together by envisioning a spherically symmetric molecule whose radius can vibrate (or breathe). By further assuming that the interaction of the target molecule with the collider is exponential with collisional separation, Bieniek & Lipson (1996) showed how a very simple expression for VT rates can be obtained by analytically summing over collisional partial waves and evaluating the thermal average over collisional energies by the method of steepest descent. The resulting mathematical expression has been shown to be highly accurate in predicting VT rates for vibrationally excited N_2, NO, and OH over large temperature ranges and levels of activation with just two fitting parameters. The astrophysically interesting molecule of H_2 and its isotopes is actually the hardest test for the breathing-sphere idea because of the large rotational spacing relative to the vibrational energies. This paper presents numerical results for the fundamental vibrational quenching $v = 1 \rightarrow 0$ of H_2, HD, and D_2 in collision with H_2. The predictions are in impressive agreement with experimental results for molecular hydrogen from 50-2000 K.

2. Analytic VT Rate Constant

The underlying assumption of the collisional model is a breathing sphere comprised of Morse oscillator states for the target molecular coordinate r perturbed by an exponential interaction in the collision coordinate R. Morse oscillators are used to model the diatomic because the vibrational eigenenrgies are $E_v = \hbar\omega_e(v + \frac{1}{2})[1 - \chi_e(v + \frac{1}{2})]$ nicely incorporate the important anharmonicity χ_e into the calculation of the change in vibrational energy $\Delta E_v = E_v - E_{v-1}$ that is transferred to translational motion. The perturbing collider will be represented as a structureless particle of mass M here (although there are methods of allowing for it to change vibrational state). Consequently, the potential operator is $V(R,r) = h_{mo}(r) + Ae^{(-\alpha R - \gamma \Delta r)}$, where A is the strength of the perturbation interaction, α is the exponential slope of the collisional perturbation, and γ is the transitional perturbation between the Morse oscillator states in the molecular stretch Δr. Because the perturbation is fundamentally caused by the collider, we can relate the α and γ by a simple proportion involving the masses (m_1 and m_2) of the two atoms in the target diatomic: $\gamma = \frac{\min(m_1, m_2)}{m_1 + m_2}\alpha$. The transitional coupling between the Morse oscillator states $U_{v,v'} = <v|e^{-\gamma \Delta r}|v'>$ needed here can be analytically evaluated with known properties of these oscillators. It turns out the strength A cancels out in the expression for the rate, so its value need not be not be known. The only other parameter besides α that is needed in the model is the characteristic collisional radius R_c of the interaction, which should be on the order of molecular diameters. All other needed quantities such as molecular masses and vibrational energy spacing can be readily obtained from standard data tables.

The analytic expression for the VT rate constant has been derived elsewhere. Although

it can be modified to incorporate the effects of multi-quantum transitions, we are only dealing with the fundamental single-quantum quenching transitions $v = 1 \rightarrow v = 0$ transition here. For single-quantum transitions $v \rightarrow v-1$, the analytic expression for the thermally averaged rate constant (in units of $length^3/time$) is:

$$k_{v \rightarrow v-1}(T) = \frac{16\pi^3\sqrt{2\pi}}{3\hbar\Gamma(\frac{3}{2})}\left(\frac{2\mu}{\hbar^2}\right)^{\frac{3}{2}}\frac{R_c^2}{\alpha^4}\frac{\Delta E_v^4}{(k_B T)^{\frac{3}{2}}}|U_{v,v-1}|^2|_2F_1(z(X_v))|^2\frac{e^{g_v(X_v)}}{\sqrt{|g_v''(X_v)|}} \tag{1}$$

where

$$g_v(x) = \beta_v[\sqrt{ax} - \sqrt{1+ax}] - \frac{\Delta E_v}{k_B T}x + ln(x) \tag{2}$$

$$\beta_v = 2\pi\frac{\sqrt{2\mu\Delta E_v}}{\hbar\alpha} \tag{3}$$

and X_v is the root of the equation

$$X_v g_v'(X_v) = \tfrac{1}{2}\sqrt{aX_v} - \tfrac{1}{2}\frac{aX_v}{\sqrt{1+aX_v}} - \frac{\Delta E_v}{\beta_v kT}X_v + \frac{1}{\beta_v} = 0 \tag{4}$$

where $a = 0.85$ and $z(x)$ is the argument of the hypergeometric function $_2F_1$:

$$z(x) = 1 + i\frac{\beta_v}{2\pi}(\sqrt{x} + \sqrt{1+x}), 1 - i\frac{\beta_v}{2\pi}(\sqrt{x} - \sqrt{1+x}), 2, 1 - \frac{|U_{v,v}|^2}{|U_{v-1,v-1}|^2} \tag{5}$$

Although all this expression may *seem* daunting, it is actually very easy to use, once one recognizes that 1) there are only two adjustable parameters: α and R_c; 2) the hypergeometric function is straightforward to calculate using a standard series expansions 3) the hypergeometric function is very nearly 1.0 for all reasonable values of its argument encountered in molecular collisions (and can just be set to one); 4) the important equation for X_v has only a single root and it can be found easily using any root-solving iterative process (even the simple Newton-Raphson method).

3. Vibrational relaxation rates for molecular hydrogen and its isotopes

The vibrational relaxation rates for $H_2(v = 1 \rightarrow 0)$ in collision with ground state H_2 have been experimentally measured by Audibert, Joffrin & Ducuing (1974) in the temperature range T=50-400 K, and by Dove & Teitelbaum (1974) for T=1350-2000 K . This experimental data was to determine the two parameters of the analytic rate constant, α and R_c. One first adjust α until the rate shape of the $k_{1\rightarrow0}$ *vs.* T curve is found, and then R_c is simply adjusted to agree with the absolute value of the rate. The values producing the best fit are: $\alpha = 2.02\text{bohr}^{-1} = 38.2\text{nm}^{-1}$ and $R_c = 5.4$ bohr $= 0.29$ nm. These same values can be used for the interaction of electronically identical HD and D_2 in isotopic substitution.

The resulting temperature dependence of quenching rates is shown in the Figure 1. Note the excellent agreement with experimental results from 100-2000 K with this two-parameter model.
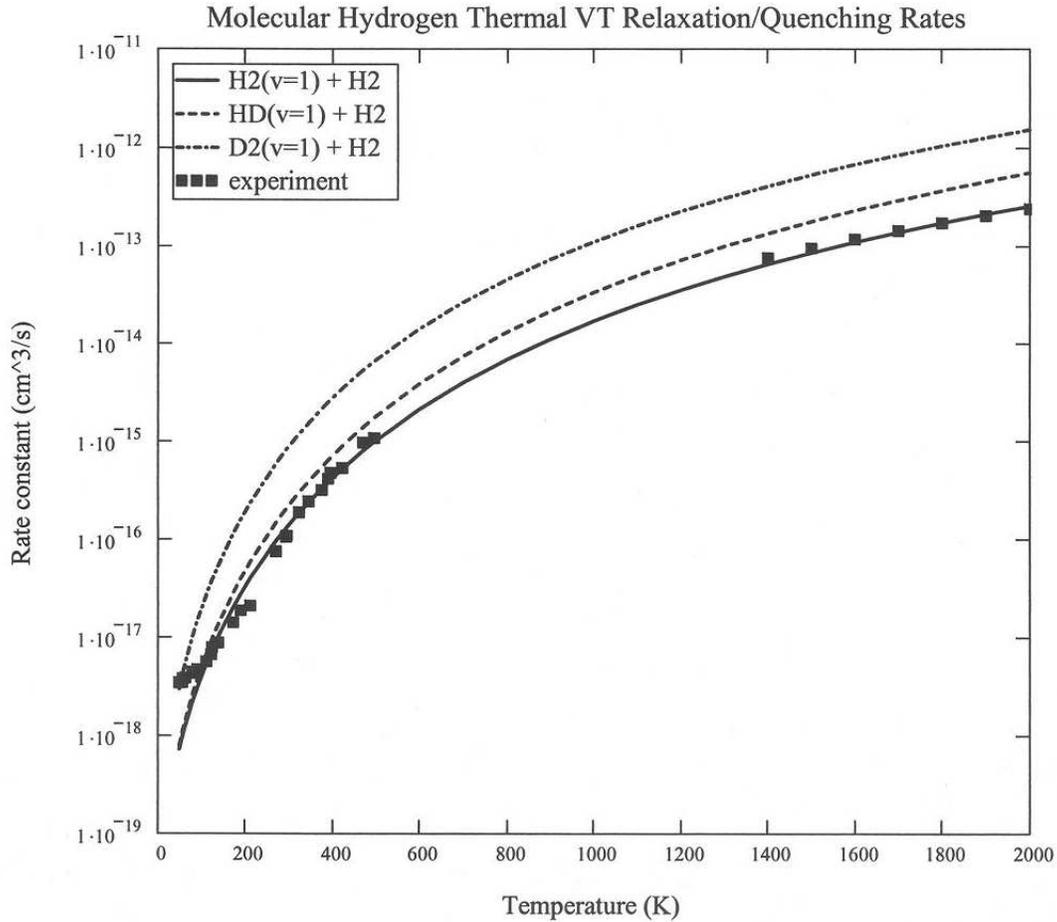

Fig. 1.— Collisional rates for vibrational relaxation of isotopes of molecular hydrogen

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