Stimulated Raman scattering measurements of H\textsubscript{2} vibration–vibration transfer

Tai Ahn, Igor Adamovich, Walter R. Lempert *

The Ohio State University, Columbus, OH 43210, United States

Received 31 October 2006; accepted 28 March 2007
Available online 7 April 2007

Abstract

We present a new set of V–V rate coefficients for vibrational levels 0–5 in H\textsubscript{2} at 300 K, measured using a stimulated Raman–spontaneous Raman pump/probe apparatus. The measured rate of the non-resonant process, H\textsubscript{2}(v = 1) + H\textsubscript{2}(v = 1) → H\textsubscript{2}(v = 0) + H\textsubscript{2}(v = 2), is consistent with the previously reported experimental value of Kreutz et al. However, semi-classical predictions of such non-resonant processes, using the identical inter-molecular potential and methodology to that given by Cacciatore and Billing, results in rates which are too slow, by a factor of approximately 3. For the ‘resonant’ V–V process, H\textsubscript{2}(v = 1) + H\textsubscript{2}(v = 0) → H\textsubscript{2}(v = 0) + H\textsubscript{2}(v = 1), the semi-classical rate is found to be too slow by an even larger factor, of approximately 30, compared to the experimental rate, but consistent with the previously reported experimental result of Farrow and Chandler. Further, unlike the semi-classical model prediction in which the (1, 1 → 2, 0) process rate is predicted to exceed that of the (1, 0 → 0, 1) process, the experimental data shows it to be a factor of approximately 2.5 less, suggesting that semi-classical methods that treat the rotational motion classically are unsuitable for the highly anharmonic H\textsubscript{2} molecule. The ratio of pure rotation and rotation–vibration Raman cross sections for scattering from levels 0 and 1 is also determined, with results which agree with calculations of Schwartz and LeRoy, but are somewhat larger than previous experimental results of Cureton.

© 2007 Elsevier B.V. All rights reserved.

Keywords: H\textsubscript{2} V–V energy transfer; H\textsubscript{2} Raman scattering cross sections; H\textsubscript{2} stimulated Raman scattering

1. Introduction

While vibrational energy loading by vibration–vibration (V–V) energy transfer plays an essential role in a wide variety of high pressure, non-equilibrium plasma processes and systems, the availability of accurate experimental V–V transfer data for such common homonuclear diatomic molecules as N\textsubscript{2}, O\textsubscript{2}, and H\textsubscript{2} has been limited by the relative difficulty of creating substantial vibrational excitation in molecules lacking a permanent dipole moment, particularly in well characterized environments which are free from interfering chemical species. To address this need, we have recently developed a pump/probe apparatus which creates vibrational excitation in the \(v = 1\) level by means of stimulated Raman scattering (SRS), and subsequently probes the temporal evolution of the vibrational distribution function (VDF) by spontaneous Raman scattering. Using this system we have recently reported new V–V rate data for N\textsubscript{2} levels \(v = 0–6\) [1], and O\textsubscript{2} levels \(v = 0–5\) [2]. For N\textsubscript{2}, excellent agreement was found between the experimental data and Master Equation modeling predictions derived using rate coefficients predicted by both the analytical forced harmonic oscillator (FHO) model of Adamovich [3], and a semi-classical model of Billing and Fisher [4]. For O\textsubscript{2}, inferred rate coefficients were in good agreement with the recently published data of Kalogerakis et al. [5], but greater than the most recent semi-classical calculations of Coletti and Billing [6].

In this paper, we present new experimental data on V–V transfer in H\textsubscript{2}, which is the simplest V–V exchange process...
that exists for a molecule–molecule interaction and therefore the system that should be most readily explained by theory. Ducuing and co-workers measured the vibration-to-translation (V–T) relaxation rate of \( H_2(v = 1) \) formed by SRS pumping of a single rotational level, \( J = 1 \) [7]

\[
H_2(v = 1) + H_2(v = 0) \rightarrow 2H_2(v = 0)
\]

Aquilanti et al. [8] have reported measurement of \( k_{1,0}^{1,0} \) (V–V) inter-species energy transfer rates from \( H_2 \) to \( D_2 \) and HD, again using stimulated Raman pumping to initially excite \( H_2(v = 1) \)

\[
H_2(v = 1) + D_2(v = 0) \rightarrow H_2(v = 0) + D_2(v = 1)
\]

In addition to measuring the rotation–rotation energy transfer rates in \( v = 1 \) and the V–V rates between \( H_2 \),\( D_2 \) and HD, Farrow and Chandler [9] also measured the \( H_2 \) “resonant” \( k_{1,0}^{1,0} \) V–V rate at 295 K.

\[
H_2(v = 1) + H_2(v = 0) \rightarrow H_2(v = 0) + H_2(v = 1)
\]

They obtained a rate coefficient value of \( 7.1 \pm 3.0 \times 10^{-14} \text{ s}^{-1} \text{ cm}^3 \) for the above reaction, which is 2–7 times faster than the reported rate for a similar process

\[
H_2(v = 2) + H_2(v = 0) \rightarrow H_2(v = 1) + H_2(v = 1)
\]

as measured by Kreutz et al. [10] \( k_{1,0}^{2,1} = (1.4) \times 10^{-14} \text{ s}^{-1} \text{ cm}^3 \) at 298 K. Farrow and Chandler attributed the difference to the near energy resonance of process (3) compared to the energy defect of \( \sim 235 \text{ cm}^{-1} \) for process (4).

To our knowledge, the only theoretical calculation of V–V rates in \( H_2 \) at 300 K have been performed by Billing and co-workers, again using semi-classical approaches. They have published a total of four sets [11–14] of theoretical calculations, an initial one [11] which gives rather fast rates, for example, \( k_{1,0}^{1,2} \approx 2 \times 10^{-14} \text{ s}^{-1} \text{ cm}^3 \), and a latter group of three [12–14], which employ similar potential surfaces and methodology and give similar results, converging, for example, on a value of \( k_{1,0}^{1,2} \approx 1 \times 10^{-14} \text{ s}^{-1} \text{ cm}^3 \). The experimental value from Ref. [10] is closer to the more recent calculations.

The present work focuses on V–V transfer in \( H_2 \) vibrational levels \( v \approx 0 \)–5. Rate coefficients are inferred by two methods, direct sequential data inversion, and comparison to Master Equation modeling. For all processes other than the resonant process

\[
H_2(1,J) + H_2(0,J') \rightarrow H_2(1,J') + H_2(2,J)
\]

the inferred rate coefficients are larger, by a factor of approximately 4, than the reported Cacciatore and Billing results [12]. For process (5), \( k_{0,1}^{0,1} \) is found to be a factor of approximately 20 greater than that reported by Cacciatore and Billing, but is in agreement, within the stated uncertainty, with the experimental value of Farrow and Chandler [9].

We also use a subset of the experimental rate data to determine the ratio of pure rotation and rotation–vibration Raman cross sections for scattering originating in vibrational levels 0 and 1. For the S(1) and S(3) pure rotational transitions, the polarizability anisotropy ratios are found to be equal to 1.6 and 1.5, respectively, values which are somewhat larger than the S(1) experimental value of 1.1 reported by Cureton et al. [15], but in agreement with the calculations of Schwartz and LeRoy [16]. For the Q(1) and S(1) rotation–vibration transitions, cross section ratios of 2.4 and 2.6 were obtained, which also agree, within the experimental uncertainty, with the calculations of Schwartz and LeRoy.

## 2. Experimental

The experimental apparatus, illustrated in Fig. 1, is similar to that described in [1,2]. Approximately 70 mJ/pulse of the second harmonic output (532 nm) of a Q-switched Nd:YAG laser is focused with a 1.5 m focal length plano-convex lens into a relatively high pressure (3 bar) stimulated Raman shifting cell [17] containing pure \( H_2 \). Approximately 10% of the incident photons are converted to the first Stokes frequency by the SRS process. The collimated SRS pump (output beam from the Raman cell), consisting of the collinear residual second harmonic and first (and second) Stokes frequency beams, is refocused into a second cell containing pure \( H_2 \) at 1 bar pressure and 300 K. The total single pulse energy of the final SRS pump pulse incident to the measurement cell is \( \sim 20 \text{ mJ} \). (Note that a substantial fraction of the incident 532 nm pulse energy is lost to stimulated Brillouin backscattering, which competes with stimulated Raman scattering in the high pressure cell). Through a second stimulated Raman scattering process, a fraction of the \( H_2 \) molecules (\( \sim \)one-third) in the focused region of the cell are initially prepared in the first excited vibrational level (\( v = 1 \)). As will be shown, due to the highly non-linear nature of the stimulated Raman conversion process, only the \( J = 1 \) rotational level is initially vibrationally excited.

The second harmonic output of a second Q-switched Nd:YAG laser, counter-propagating to the SRS pump beam, probes the excited volume by means of spontaneous vibrational (Q-branch) and pure rotational (S-branch) Raman scattering. Under the employed conditions, mass diffusion is the principal loss mechanism of vibrational quanta (as opposed to V–T relaxation), which is confirmed by radial resolution of the pumped volume using a probe beam with diameter significantly smaller than that of the pump. In practice, this is achieved by translation of the SRS pump beam, while maintaining a fixed probe, in order to maintain constant scattering collection efficiency. The Raman signal is spectrally resolved using a 0.3 m spectrometer and collected by an ICCD camera. For pure rotational scattering, the time delay between the pumping and probing is varied between 30 ns and 3 \( \mu \text{s} \) in order to determine the time evolution of the rotational and/or vibrational level populations. For vibrational scattering, time delays shorter than \( \sim 100 \text{ ns} \) result in stray scattering of the Stokes com-
ponent of the SRS pump interfering with the true Stokes probe signal.

Relative populations are inferred from inspection of the peak heights of the resolved Q- and S-branch spectra and are put on an absolute scale by calibration with room temperature spectra in which the entire population is in the \( v = 0 \) level, with equilibrium rotational distribution. As will be described in Section 4, \( v \)-level dependence of the Raman cross sections are based on the polarizability matrix elements of Schwartz and Leroy [16]. Uncertainty in the fractional populations is estimated to be 0.02, 0.02, 0.005, 0.003, 0.002, and 0.001, respectively, for levels \( v = 0 \)–5.

As will also be described in Section 4, intensity ratios of and SRS pumped and non-pumped pure rotational spectra also allow us to determine some rotation and rotation–vibration Raman cross section ratios. This measurement will be described in more detail in Section 4.

3. Kinetic modeling

As in our previous work [1,2], rate coefficients for single quantum V–V transfer are inferred from experimental vibrational distribution function (VDF) data using the Master Equation approach, which is summarized by the set of equations:

\[
\frac{dN_{i,v}}{dt} = \nu V_{i,v} + \nu T_{i,v} + \nu E_{i,v} + \nu D_{i,v} + \nu P_{L,i,v} + D_{i,v} N_{i,v}
\]

\[
\rho c_p \frac{dT}{dt} = \nu T \nu^2 T + HVR
\]

where \( D_{i,v} N_{i,v} \) and \( \nu T \nu^2 T \) represent, respectively, mass diffusion and conduction heat transfer in the radial direction, and HVR is an energy source term due to all vibrational relaxation processes. Other terms are discussed individually below. Explicit expressions for each of the terms in Eq. (6) can be found in Flament et al. [18].

While not presented, spontaneous Raman (S-branch) rotation–vibration spectra, obtained prior and immediately after the SRS pump pulse, confirmed negligible (\( \lesssim 10 \) K) temperature increase accompanying vibrational excitation so that \( T \) can be regarded as constant, eliminating Eq. (6b). Since direct collisional transfer from the ground to excited electronic states is exceedingly slow at room temperature, the vibration to electronic energy transfer term, \( V–E \), is assumed negligible. Similarly, since \( \text{H}_2 \) does not have a permanent dipole moment, the infrared spontaneous radiative decay term, \( \text{SRD}_{i,v} \), is also omitted. The laser absorption term, \( \text{PL}_{i,v} \), creates the initial excitation condition for population of vibrational levels \( v = 0 \) and 1, which is determined experimentally.

The \( \text{H}_2–\text{H}_2 \) V–V transfer rate for vibrational level \( v \) is written as

\[
\nu V = \sum_{v'} \left[ k_{i,v \rightarrow v} N_{i,v} \right] + k_{i,v \rightarrow v+1} N_{i,v} - \left( k_{i,v \rightarrow v-1} + k_{i,v+1} N_{i,v} \right) N_{i,v}
\]

(7)

where the term \( k_{i,v \rightarrow v+1} \) is the rate coefficient for the following reaction:

\[
\text{H}_2(v) + \text{H}_2(v') \xrightarrow{\text{Collisions}} \text{H}_2(v+1) + \text{H}_2(v-1)
\]

(8)
As we will show in the next section, although predictions from Cacciatore and Billing [12] and Kreutz et al. [10] suggest that the H$_2$–H$_2$ V–T rates are significant, even for low vibrational levels, it was found that accurate simulation of the rise time of the vibrational populations required only consideration of V–V transfer, even in the presence of other, for $v \geq 2$, non-negligible decay mechanisms. Therefore, kinetic modeling considered only V–V processes and mass diffusion. This assumption is further validated by radialy resolved data, such as that of Fig. 2, which shows the measured and predicted profile of the $v = 1$ absolute population for very short (30 ns) and longer (3 $\mu$s) pump/probe time delays. The model assumes the initial Raman pumped $v = 1$ spatial distribution to be Gaussian and symmetric about the pump laser propagation axis, $N(v = 1, r) = N(v = 1, r = 0) \times \exp\left(-\frac{r^2}{2\sigma^2}\right)$ with $\sigma = 76$ $\mu$m, based on experimental determination of the pump/probe beam spatial profiles [1]. The probe laser beam radius is considerably smaller, less than 10 $\mu$m. For such cases, the results of the kinetic modeling are essentially identical to those assuming an infinitely small probe beam radius. It can be seen that the predicted profile, after 3 $\mu$s is consistent with the experimental results. Note that the shape of the profile depends only upon mass diffusion, whereas the absolute level population is dominated by V–V transfer kinetics.

Note that the calculation in Fig. 2 is based on V–V rates given in column 1 of Table 2, inference of which will be described in Section 4.

As with our recently published O$_2$ V–V studies [2], we employ two approaches for inference of rate coefficients, $k_{v',v-1}^{v,v+1}$, from the experimental data. The first approach is to compute a complete set of coefficients employing semi-classical trajectory calculations and to compare the predicted vibrational distribution functions with the experimental data. This has the advantage that it incorporates a full set of forward and backward processes into the modeling and that it produces a complete set of rates coefficients. The disadvantage is that the inferred “best fit” rates are constrained to relative values resulting from the semi-classical prediction. As stated previously, V–V rates in H$_2$ at 300 K have been calculated by Billing and co-workers, who have reported a total of four sets [11–14], of which the latter three are in good agreement with one another.

### Table 1

<table>
<thead>
<tr>
<th>$v$</th>
<th>This work semi-classical</th>
<th>Cacciatore and Billing [12]$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.36</td>
<td>0.43</td>
</tr>
<tr>
<td>1</td>
<td>1.3</td>
<td>0.96</td>
</tr>
<tr>
<td>2</td>
<td>2.8</td>
<td>1.7</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>5.3</td>
<td>3.2</td>
</tr>
<tr>
<td>5</td>
<td>5.3</td>
<td>3.2</td>
</tr>
<tr>
<td>6</td>
<td>4.6</td>
<td>2.4</td>
</tr>
<tr>
<td>7</td>
<td>3.6</td>
<td>1.6</td>
</tr>
<tr>
<td>8</td>
<td>2.4</td>
<td>1.0</td>
</tr>
<tr>
<td>9</td>
<td>1.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

$^*$ Rates estimated from Fig. 5 of Ref. [12].

To obtain a complete set of rates for Master Equation modeling, in the present work the rates reported in Cacciatore and Billing [12] were recalculated using the same inter-molecular potential. For this, we used a semi-classical trajectory code DIDIAV developed by Billing [19]. In the calculations, V–V cross sections were calculated for 17 values of total collision energy from 100 to 10,000 cm$^{-1}$, for 1000 randomly picked trajectories per energy, and averaged over the Boltzmann distribution to obtain the V–V rates. Ref. [12] was selected because it gives explicit values for the largest number of rates, $k_{v,0}^{v,1}$, for $v = 0$–9. As can be seen in Table 1, the recalculated and original rate coefficients exhibit a similar trend, increasing monotonically from $v = 0$ to $v = 5$, and then decreasing smoothly. For levels $v = 1$–5, which covers the range of experimental “non-resonant” data to be presented here, the recalculated values are larger than the originally published values, by an approximately constant factor of ~30%, a discrepancy which is of similar magnitude to that for our previously published N$_2$ and O$_2$ studies [1,2]. For higher $v$ levels, the recalculated rates drop off somewhat less rapidly, with increasing $v$, than the original reported rates. While the
reason for these discrepancies is not clearly understood, it is likely related to the choice of the size of the phase space region, such as the value of maximum collision orbital angular momentum used in the present semi-classical calculations. We note that both calculations predict the value of $k^{1.0}_{1.0}$ to be less than the value for $k^{1.1}_{1.0}$, a result, as will be shown, which does not agree with the data.

As will also be shown, the recalculated rate coefficients had to be multiplied, somewhat arbitrarily, by a constant factor of approximately 2.9 to achieve best agreement with the experimental data. For brevity, in the discussion which follows we shall often refer to these recalculated rates, as “Cacciatoore and Billing rates,” since they were obtained with the identical potential and methodology.

The second approach extracts rate coefficients $k^{v_{n+1}}_{v_n}$ directly from the data by sequentially, with increasing $v$, fitting the rise portion of each experimental VDF. This has the advantage of not imposing any a priori constraints on the relative magnitude of the rate coefficients, but is subject to systematic error due to neglect of the coupling with higher $v$ processes, such as $k^{3.2}_{2.1}$ which are not included in the analysis. Uncertainty is estimated by means of sensitivity analysis. As we will show, the two approaches agree to better than the estimated ±20% uncertainty, for the rate coefficient $k^{1.2}_{1.0}$.

4. Results

4.1. Population data and master equation analysis

SRS pumping is performed in pure H$_2$ at 1 bar pressure and 300 K temperature. In addition to using spontaneous vibrational Raman Q-branch ($v, J \rightarrow v + 1, J$) transitions to probe the time dependent population of vibrational levels, pure rotational S-branch, ($v, J \rightarrow v, J + 2$) transitions are also used. It is not possible, with our apparatus, to employ spontaneous pure rotational S-branch scattering for N$_2$ and O$_2$ because the $v, J \rightarrow v, J + 2$ transitions with the same $J$, but from different vibrational levels overlap in frequency, to within the experimental resolution of our spectrometer. However, in H$_2$, due to the much larger rotation ($\beta_c$) and rotation–vibration coupling ($\alpha_c$) energies, the pure rotational S-branch transitions have much larger, very readily resolved, splitting.

Fig. 3 shows Q-branch Raman spectra obtained at several time delays between the pump and probe pulses. Levels as high as $v = 4$ are readily observed. Fig. 4 shows a magnified intensity axis, revealing the small but measurable population in higher vibrational levels. Figs. 5 and 6 show pure rotational S-branch Raman spectra at several time delays analogous to Figs. 3 and 4, respectively. The

![Fig. 3](image_url)

Fig. 3. Spontaneous Q-branch Raman signal of Raman pumped H$_2$ at 100 ns, 500 ns, 1.6 µs, and 3 µs after Raman pumping. Pressure equals 1 bar and temperature equals 300 K.
intensity scales in all spectra are arbitrary and do not relate from one spectrum to another. Although the S-branch spectra exhibit lower signal to noise, compared to the Q-branch, they have the advantage of being rotationally resolved. As will be shown, this enables the measurement of the rate of the resonant process (3).

As alluded to previously, polarizability matrix elements of Schwartz and LeRoy [16] are used to obtain Raman cross sections for both the Q-branch and S-branch signals. It will be shown that their calculated values are in agreement with our experimental results.

Fig. 7 shows a comparison of experimental and modeled values for the population of vibrational levels $v = 0–3$. The experimental values are extracted from the vibrational Q-branch spectra of Figs. 3 and 4, whereas the modeling is based on the recalculated semi-classical rates employing...
the potential of Cacciatore and Billing. It is clear that the semi-classically derived rates predict a less rapid temporal evolution (the bold solid line) than is observed experimentally. The thin solid line shows the predictions using the Cacciatore and Billing derived rate coefficients multiplied by a constant factor of 2.9, which are seen to give much better agreement, particularly for the initial rise portion of the data. The dotted line and the dashed line correspond to predictions using 2.9 times the Cacciatore and Billing rates increased/decreased by 30%, respectively. It can be seen that these curves approximately bracket the uncertainty (2\(\sigma\)) in the experimental data. From this sensitivity analysis we assign an uncertainty in the inferred rates of approximately ±30%. We note,
however, that the population of levels 4 and 5, decay more rapidly than predicted, possibly due to the influence of V–T processes that become significant at higher vibrational levels, or due to collision induced dissociation

\[ \text{H}_2(v \geq 5) + \text{H}_2(v \geq 5) \rightarrow \text{H}_2 + 2\text{H}, \tag{9} \]

where it is noted that the vibrational energy of \( \text{H}_2 \) in vibrational level \( v = 5 \) is greater than 50% of the dissociation energy.

As stated previously, we have also performed pure rotational S-branch \((v, J \rightarrow v, J + 2)\) probing. Fig. 9, which compares VDFs derived from the Q-branch data of Fig. 3 and S-branch data of Fig. 5, demonstrates that both methods give essentially identical results. Considering all the data, the value of the rate coefficient for the process

\[ \text{H}_2(v = 1) + \text{H}_2(v = 1) \rightarrow \frac{k_{1,1}^{1,2}}{k_{0,1}^{1,2}} \text{H}_2(v = 2) + \text{H}_2(v = 0) \tag{10} \]

gives best agreement with experiment is \( k_{1,0}^{1,2} = 3.8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \). From detailed balance, the rate coefficient for the reverse process is, therefore, \( k_{0,1}^{2,1} = 1.3 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \), which is within the range reported in [10].

\[ k_{0,1}^{2,1} = (1.4) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}. \]

Fig. 10 shows the total ortho/para state populations in vibrational levels \( v = 0 \) and 1 as function of pump/probe time delay. Due to the extreme non-linear nature of the conversion process in the stimulated Raman shifting cell, the SRS Raman pump pulse drives only the transition between \( \text{H}_2(v = 0, J = 1) \) and \( \text{H}_2(v = 1, J = 1) \). Therefore, immediately after the pulse, all molecules in \( v = 1 \) will have ortho parity \((J \text{ odd, specifically } J = 1)\). However, as can be seen in the 30 ns delay spectrum of Fig. 5, the nearly gas kinetic rotational energy transfer rate for collisions with \( \Delta J = 2 \) (parity conserving), results in the \( v = 1, J = 3 \) state becoming quickly populated.

\[ o-H_2(v = 1, J = 1) + H_2 \rightarrow o-H_2(v = 1, J = 3) + H_2 \tag{11} \]

Since parity changing collisions are strongly disallowed, true ortho–para conversion does not occur on time scales relevant to the measurements presented here. As a result, states in \( v = 1 \) with even \( J \) values can only be populated by “resonant” V–V processes, such as

\[ H_2(v = 1, J = 1) + H_2(v = 0, J = 0, 2) \rightarrow H_2(v = 0, J = 1) + H_2(v = 1, J = 0, 2) \tag{12} \]
so that the rise in population of molecules with para parity (even J) in vibrational level \( v = 1 \) will depend on the rate of the process

\[
\text{H}_2(v = 1) + \text{H}_2(v = 0) \rightarrow \text{H}_2(v = 0) + \text{H}_2(v = 1)
\]

(13)

From Fig. 10, it is clear that the recalculated Cacciatore and Billing values for this process predicts rates that are much slower, by more than an order of magnitude, than that observed in the experiment, in contrast to the kinetics of the “non-resonant” V–V processes in which the recalculated rate coefficients of Cacciatore and Billing were found to underestimate the V–V rates by a factor of approximately 3–4. The solid line, which corresponds to the best agreement with experimental data, uses a rate coefficient value which is 28 times the value of the Cacciatore and Billing rate, specifically \( k_{0,1}^{1.0} = 9.9 \times 10^{-14} \text{cm}^3 \text{s}^{-1} \). While not shown in Fig. 10, a sensitivity analysis similar to that illustrated in Figs. 7 and 8 also resulted in an estimated uncertainty of ±30%, making the present work consistent with the anomalously high rate of this reaction to its near zero energy defect, as compared to the energy defect of 235 cm\(^{-1}\) for the \( k_{0,1}^{1.0} \) process. We stress that regardless of energy defect, semi-classical calculations predict the value of \( k_{0,1}^{7.0} \) to be lower than that of \( k_{0,1}^{1.0} \), while our experimental results, and those of others, demonstrate otherwise (\( k_{0,1}^{7.0} = 9.9 \times 10^{-14} \text{cm}^3 \text{s}^{-1} > k_{0,1}^{1.0} = 4.5 \times 10^{-14} \text{cm}^3 \text{s}^{-1} \)). This suggests that semi-classical methods, which treat the rotational motion classically, rather than quantum mechanically, are not truly adequate in calculating V–V rate coefficients for \( \text{H}_2 \), particularly the relative rate of the “resonant” \( k_{0,1}^{1.0} \) process to that of the “non-resonant” rates. We speculate that this is due to the relatively large rotational energy spacing in \( \text{H}_2 \), which is comparable to \( k_B T \) (\( B_0 = 60 \text{ cm}^{-1} \) for \( \text{H}_2 \)), in contrast to the rotational energy (\( B_r \approx 2 \text{ cm}^{-1} \)) for \( \text{O}_2 \) and \( \text{N}_2 \).

The rates inferred from comparison of the present data to semi-classical prediction are summarized in the first column of Table 2.

**Fig. 10.** Fraction of total odd \( J, \) ortho (left) and even \( J, \) para (right) molecules in vibrational levels \( v = 0 \) (open circles) and 1 (filled circles). Thin solid lines are predictions using recalculated Cacciatore and Billing rate of \( k_{0,1}^{6.5} = 3.6 \times 10^{-15} \), while the bold solid line uses this rate multiplied by a factor of 28.

**Table 2**

<table>
<thead>
<tr>
<th>( v )</th>
<th>This work semi-classical</th>
<th>This work data inversion</th>
<th>Farrow and Chandler [9]</th>
<th>Kreutz et al. [10]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( 1.0 \pm 0.3 )</td>
<td>( 9.9 \pm 2 )</td>
<td>4–10</td>
<td>3–12</td>
</tr>
<tr>
<td>1</td>
<td>( 3.8 \pm 1.3 )</td>
<td>( 3.8 \pm 0.8 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( 8.2 \pm 2.4 )</td>
<td>( 10 \pm 2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( 13 \pm 3.6 )</td>
<td>( 18 \pm 5 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( 15 \pm 4.5 )</td>
<td>( 25 \pm 10 )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note failure of semi-classical scaling to predict \( k_{0,1}^{6.5} \) rate.

### 4.2. Data inversion

As an alternative to reliance on semi-classical predictions, we have inferred rates directly from the data, in a manner similar to that utilized in previous \( \text{O}_2 \) V–V measurements [2]. As a starting point, we note that for times immediately following the initial SRS excitation, where only levels 0 and 1 are populated, the only population modifying process is (10), which populates level \( v = 2 \). For time scales such that mass diffusion can be ignored, the population of \( v = 1 \) evolves according to the simple second order kinetic expression

\[
\frac{1}{N(v = 1, t)} \approx \frac{1}{N(v = 1, t = 0)} + 2k_{1,0}^{2,1} t.
\]

(14)

Fig. 11a shows a plot of \( 1/N(v = 1) \) versus \( t \). The solid line is a least squares fit of the linear portion of the data (up to time delay of 1 \( \mu s \)) with best fit rate coefficient \( k_{1,0}^{2,1} = 4.7 \times 10^{-14} \text{cm}^3 \text{s}^{-1} \) obtained from the slope of the fitted line. We note that this value is somewhat higher than the value inferred in the previous section. Of course in addition to ignoring mass diffusion, Eq. (14) also ignores the reverse of process (10), which acts to refill the \( v = 1 \) level. Fig. 11b shows the full Master Equation prediction for the population of the \( v = 1 \) level as a function of time, where the initial value was determined by extrapolation of the least squares line in Fig. 11a to \( t = 0 \). The solid curve is the prediction for a value of \( k_{1,0}^{2,1} = 3.8 \times 10^{-14} \), whereas the dashed and dotted correspond to values of \( 2.7 \times 10^{-14} \), and \( 5.0 \times 10^{-14} \), respectively. These values, which were
obtained from a trial and error procedure incorporating both the forward and reverse of process (10), represent the best “fit” value, and an estimate of the range of values which bracket the approximate experimental uncertainty in the data points. Note that the inferred best value, $k_{1,0}^{12} = 3.8 \times 10^{-14}$, is essentially identical to that inferred from the semi-classical rates (which were constrained to simultaneously fit all of the data), and $\sim 20\%$ lower than that resulting from a fit of the data to Eq. (14).

The procedure for inference of rates for higher vibrational levels needs to incorporate the inherent coupling of all relevant V–V processes. For example, the rise of population in level 3 is dominated by the forward and reverse process,

$$H_2(2) + H_2(1) \rightarrow H_2(3) + H_2(0)$$  \hspace{1cm} (15)

the rates for which depend explicitly upon the time-dependent population of levels $v = 0–3$. Our approach is to first fix the value of $k_{1,0}^{12} = 3.8 \times 10^{-14}$ cm$^3$ s$^{-1}$, determined from the $v = 1$ and $v = 2$ population data, and then impose detailed balance to model the rise of $v = 3$, assuming that the rate of the forward and reverse of process (15) are related by the equilibrium constant. Such a trial and error procedure is performed sequentially, resulting in an initial set of rate coefficients $k_{v+1}^{v}$. For example, the initial simulation of level $v = 4$ is based on fixing rate coefficients determined from the $v = 1$, 2, and 3 data, while adjusting $k_{3,0}^{3,4}$ to give best agreement. Once $k_{3,0}^{3,4}$ is fixed, $k_{1,0}^{5}$ is adjusted to best simulate the $v = 5$ data, etc. After an initial set of rate coefficients have been determined, the procedure is repeated, but including the higher vibrational level processes which were ignored previously. The addition of higher $v$ processes changes, somewhat ($\sim 5–10\%$, or less) the predicted rate of population rise. The preliminary rate coefficient set is iterated until a set is converged upon which simultaneously best fits all the available data.

Such a simulation analysis has been performed for levels $v = 2–5$, the results of which are illustrated in Fig. 12. In each case the solid curve represents the best “fit” to the data and the dashed and dotted curves, analogous to Fig. 11, to predictions in which the best fit rates have been modified by approximately $\pm 30\%$, resulting in predictions which approximately bracket the experimental uncertainty in the data.

The inferred rates (rounded to two significant figures) and estimated uncertainty (rounded to one significant figure) resulting from this data inversion procedure, are presented in the second column of Table 2. We note that the inversion procedure, while having the advantage of not relying on a semi-classical calculation of the relative v-dependence, does introduce more uncertainty in the rates for higher values of $v$, due to error propagation, and the fact that processes such as $(3,2 \rightarrow 4,1)$ are not included in the simulation. An estimate of these effects is reflected in the estimated uncertainty limits given in column 2 of Table 2.

4.3. Determination of Raman cross sections for $v = 1$

While not the primary focus of the present study, we note that the experimental data can also be used to determine Raman cross section ratios for scattering of $H_2$ molecules originating in vibrational levels 1 and 0. In this regard we note that due to the large anharmonicity of the $H_2$ molecule, the vibrational scattering cross section dependence upon vibrational level is expected to deviate significantly from the $\sigma_{v}$ proportional to $v/v + 1$ scaling, for anti-Stokes/Stokes respectively, of harmonic oscillator – rigid rotors [20]. As described in many basic texts on Raman scattering [20,21] the intensity of a transition involving a change in rotational level is directly proportional to the square of the anisotropic part of the polarizability, generally denoted by the symbol $\gamma_{J',J'}$. For transitions involving no change in $J$ (i.e., vibrational Q-branches), the total intensity, which is the sum of the collected scattering with polarization parallel and perpendicular to the incident beam polarization direction, has contributions from both the isotropic and anisotropic polarizability components.

Fig. 11. (a) Inverse of the time-dependent population of $v = 1$. Filled circles indicate experimental data. Solid line is a least squares fit to Eq. (14) taking into account only the initial linear portion of the data. The dashed line is the prediction using $k_{1,0}^{12} = 1.3 \times 10^{-14}$ cm$^3$ s$^{-1}$, the recalculated Cacciatore and Billing value. (b) Time-dependent population of $v = 1$ for assumed values of $k_{1,0}^{12} = 3.8 \times 10^{-14}$ (solid), 2.7E–14 (dashed), and 5.0E–14 (dotted).
Augustine and co-workers [15] have reported an experimental determination of the Raman polarizability anisotropy for $\text{H}_2(v=1)$ pure rotational scattering, using a method similar that employed in this work. They pumped the Q(1) ($v=0, J=1 \rightarrow v=1, J=1$) Q-branch transition to saturation, achieving an assumed, but not directly measured, 1:1 population ratio between the ground vibrational level and the upper level. They then measured the intensity ratio of the pure rotational S(1) transitions ($J=1 \rightarrow J=3$) from the two vibrational levels, $v=0$ and 1. If it is assumed that the ground level number density of the two transitions are equal, and if there is no rotational redistribution between the pumping and the probing, then the detected probe signal ratio is directly proportional to the square of the polarizability anisotropy element, $\langle \gamma_{11,13} \rangle^2/\langle \gamma_{01,03} \rangle^2$. Using this approach, Augustine reported a value of 1.115, which is considerably lower that the calculated value of 1.5 reported by Schwartz and Leroy [16].

It is clear from our experimental data that we do not completely saturate the Raman pumping transition. However, by comparing the detected probe signal prior to and after SRS pumping, the cross section ratios can nonetheless be determined. Focusing, initially, on the pure rotational spectra, the intensity ratio of the S(1) transition in the cold spectrum to that in the Raman pumped spectrum with zero time delay will be equal to the ratio of the $v=0, J=1$ population before and immediately after Raman pumping. In addition, immediately after the SRS pump all population lost from $v=0, J=1$ will reside in $v=1, J=1$. However, due to extremely rapid rotational energy transfer (RET), which occurs within our minimum pump/probe time delay of 30 ns, this nascent population ratio cannot be measured in our experiment. Nonetheless, even if we include the effect of RET, all population lost from the cold $v=0$, $J=1$ level will reside in levels $J=1$ or $J=3$ of the pumped $v=1$ vibrational level. This leads to the following set of equations:

$$\frac{I_{\text{pumped}}(v=0, J=1)}{I_{\text{cold}}(v=0, J=1)} = \frac{N_{\text{pumped}}(v=0, J=1)}{N_{\text{cold}}(v=0, J=1)}$$

(16)

$$\frac{I_{\text{pumped}}(v=1, J=1)}{I_{\text{pumped}}(v=0, J=1)} = \frac{\langle \gamma_{11,13} \rangle^2}{\langle \gamma_{01,03} \rangle^2} \frac{N_{\text{pumped}}(v=1, J=1)}{N_{\text{pumped}}(v=0, J=1)}$$

(17)
If we assume that rapid RET leads to a thermal equilibrium between the $J = 1$ and $3$ levels in the $v = 0$ and $v = 1$ levels of both the cold and pumped spectra, then we can eliminate all terms in (18) involving $J = 3$. At 300 K,

\[ \frac{N_i(v = 0, J = 3)}{N_i(v = 0, J = 1)} = \begin{cases} 1 & (19a) \\ 7.18 & (19b) \end{cases} \]

where the subscript $i$ refers to either cold or pumped spectra. Note that the difference in Boltzmann fractions between the $v = 0$ and $1$ levels is a consequence of the significant rotation–vibration coupling of H$_2$. Substitution of (18) and (19) into (17) gives:

\[
\frac{I_{\text{pumped}}(v = 1, J = 1)}{I_{\text{pumped}}(v = 0, J = 1)} = \left( \frac{\gamma_{11,13}}{\gamma_{01,03}} \right)^2 \left( 1 + \frac{1}{7.18} \right) \left( 1 + \frac{1}{6.24} \right) \left( \frac{I_{\text{cold}}(v = 0, J = 1)}{I_{\text{cold}}(v = 0, J = 1)} - 1 \right)
\]

(20)

Fig. 13 shows the rotational S-branch, $v, J = 1 \rightarrow v, J = 3$ spectrum before (upper) and 30 ns after (lower) Raman pumping (note the $v = 1, J = 3$ transition at $\sim 559$ nm in the pumped spectrum). Substitution of the observed $J = 1$ intensity ratios into Eq. (20) yields a value of $\langle \gamma_{11,13} \rangle^2 / \langle \gamma_{01,03} \rangle^2$ equal to $1.6 \pm 0.3$, which is higher than the value of Augustine, but in agreement with the value of Schwartz and LeRoy. A similar analysis for $\langle \gamma_{13,13} \rangle^2 / \langle \gamma_{03,03} \rangle^2$ resulted in a value of $1.5 \pm 0.3$, in agreement with the value of 1.5 given by Schwartz and LeRoy.

Fig. 14 shows vibrational Q-branch spectra before and 100 ns after Raman pumping. Since the Q-branches are unresolved, it is only possible to determine the total cross section ratio, assuming no $J$ level dependence. Correcting for the $\sim1\%$ population in level $v = 2$ in the $\Delta t = 100$ ns spectrum (see Fig. 7), we find $\langle \gamma_{11,11} \rangle / \langle \gamma_{11,10} \rangle = 2.4 \pm 0.4$. For comparison, the cross section ratio predicted by LeRoy is 2.16, which while lower than our value, is within the estimated uncertainty.

Finally, Fig. 15 shows vibrational S-branch ($v, J \rightarrow v + 1, J + 2$) Raman scattering transitions before and 100 ns after Raman pumping, where the transitions are situated on the high wavelength tail wing of the $v = 0 \rightarrow v = 1$ Q-branch transition. (Note that the vibrational S-branch peaks from vibrational levels greater than 1 are too weak to be detected in the presence of the intense Q-branch peak.) By analysis similar to that for pure rotational spectra, we determine a value of $\langle \gamma_{11,23} \rangle^2 / \langle \gamma_{11,13} \rangle^2$ equal to $2.6 \pm 0.4$, which while higher than the value of 2.4 pre-
dicted by LeRoy, again agrees within the experimental uncertainty.

Table 3 summarizes the Raman cross section data.

5. Conclusions

We have presented a new set of V–V energy transfer data for H2 at 300 K measured using a stimulated Raman–spontaneous Raman pump/probe technique. Approximately one-third of the molecules are initially prepared in the first vibrationally excited level, \( v=1 \), by means of stimulated Raman scattering. Spontaneous pure rotational (S-branch) and rotation–vibration (Q-branch) Raman scattering is used to probe the temporal evolution of the vibrational distribution function for levels as high as \( v=5 \), with identical results to within the experimental uncertainty. Absolute rate coefficients are inferred by two methods, both of which are based on comparison of the experimental VDF data with predictions of Master Equation modeling. The first method is using V–V rates recalculated using the potential and methodology by Cacciatore and Billing [12], and scaled by a constant factor. The second approach extracts rate coefficients directly from the data, using sequential data inversion. The two methods inferred rate coefficients which agreed, within estimated experimental uncertainty.

The measured rate of the non-resonant process, \( \text{H}_2(\nu = 1) + \text{H}_2(\nu = 0) \rightarrow \text{H}_2(\nu = 0) + \text{H}_2(\nu = 1) \), is consistent with the previously reported experimental value of Kreutz et al. However, for non-resonant processes, comparison of the experimental rates with the results of semi-classical calculations showed the theoretical rates to be too slow, by a factor of approximately 3. The semi-classical rate for the “resonant” V–V process, \( \text{H}_2(\nu = 1) + \text{H}_2(\nu = 0) \rightarrow \text{H}_2(\nu = 0) + \text{H}_2(\nu = 1) \), was also found to be too slow, by approximately a factor of 30, compared to the experimental rate measured using pure rotational Raman, but consistent with the previously reported experimental result of Farrow and Chandler. Further, unlike the semi-classical model prediction in which the value of \( k_{\text{res}}^{0,0} \) is predicted to exceed that \( k_{\text{res}}^{1,1} \), the experimental data shows it to be a factor of approximately 2.5 less. This suggests that the semi-classical calculation methods that treat the rotational motion classically may be unsuitable for H2, due presumably to the rotational energy level spacing comparable to \( k_{\text{B}}T \).

The data is also used to determine Raman cross section ratios for scattering of H2 molecules originating in vibrational levels 1 and 0. For the S(1) and S(3) pure rotational transitions, the polarizability anisotropy ratios are found to be equal to 1.6 and 1.5, respectively, values which are somewhat larger than the S(1) experimental value of 1.1 reported by Cureton, but in agreement with the calculations of Schwartz and LeRoy. For the Q(1) and S(1) rotation–vibration transitions, cross section ratios of 2.4 and 2.6 were obtained, which also agree, within the experimental uncertainty, with the calculations of Schwartz and LeRoy.

Acknowledgements


References