False estimates of stimulated Raman pumping efficiency caused by the optical Stark effect

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One technique for measuring the fraction of molecules pumped to the excited state in stimulated Raman pumping (SRP) is to record the depletion of molecules in the lower state by resonance enhanced multiphoton ionization (REMPI). The presence of electric fields on the order of 10^7 V/cm arising from the pulsed SRP laser beams is sufficient to shift the line position of the REMPI transition to such an extent that the estimate of the pumping efficiency is overestimated unless this shift is accounted for. © *2011 American Institute of Physics*. [doi:10.1063/1.3601923]

Stimulated Raman pumping (SRP) is widely used as a method to prepare molecules in specific rovibrational states, primarily for scattering experiments. In SRP, two laser beams are used whose energy difference is tuned to a Raman allowed transition. The SRP process has an advantage over direct IR absorption in which it does not require that the molecule possess a dipole moment and therefore has often been applied to pump nonpolar molecules. The first account of SRP in the gas-phase is by Hagenlocker and Rado[1] who used it to prepare H_2, D_2, and CH_4 with one quantum of vibrational excitation. Since then, several groups have reported the preparation of rovibrationally excited molecules with SRP for various purposes. Reck and co-workers[2] report a convenient way to prepare and detect H_2 ($v = 1, j = 1$) using a single laser by Raman shifting the 193 nm output of an ArF laser in a Raman cell to produce 210 nm light. Mikulecky and Gericke,[3] and Han, Chen, and Weiner[4] have prepared H_2 ($v = 1$) to study the reaction dynamics of O + H_2 ($v = 1$). In addition, Zare and co-workers[5–9] have prepared vibrationally excited H_2, HD, and CH_4 using SRP for reactive scattering experiments with D and Cl atoms. They also used SRP to prepare aligned samples of HD and D_2, and have characterized the time dependence of the alignment, due to hyperfine depolarization, with [2+1] resonance enhanced multiphoton ionization.[10,11] Aligned samples of C_2H_2 have been prepared by Zacharias and co-workers[12] using SRP, while Sitz and Farrow[13] have reported on the rotational energy transfer rates of N_2 ($v = 1$) as well as the preparation and decay of alignment of the same molecule.[14] The laboratories of Sitz and Rizzo have looked extensively at the effect of SRP-prepared vibrational excitation on the gas-surface scattering of H_2 ($v = 1, j = 1$) from Cu(100) (Refs. 15–17) and Pd(111) (Ref. 18) and CH_4 ($v_1 = 1$) from Ni(100) (Ref. 19). Crim and co-workers[20] have prepared HNCO ($v_1 = 1$ or $v_3 = 1$) by SRP and investigated the effect of vibrational excitation on photodissociation branching ratios. The first account of SRP in preparing a gas-phase negative ion C_2^- has been reported by Neumark and co-workers.[21]

For some experiments, it is necessary to quantify the fraction f of molecules that are pumped to the excited state. This quantity has been estimated by Kliner, Adelman, and Zare[6] (KAZ) and Augustine and co-workers[22] for the $Q_{10}(1)$ transition of H_2, and Sitz and Farrow[14] (SF) for the $Q_{10}(6)$ transition of N_2. The method used to measure the SRP efficiency in the case of SF and KAZ is similar but with important differences. Resonance-enhanced multiphoton ionization (REMPI) is first used to detect H_2 ($v = 0, j = 1$) or N_2 ($v = 0, j = 6$) using the $Q(1)$ line of the (0,0) band of the H_2 $E,F\ ^1\Sigma_g^+$–$X\ ^1\Sigma_g^+$ transition or the $O(6)$ line of the (1,0) band of the N_2 $a^1\Pi_g$–$X\ ^1\Sigma_g^+$ transition, respectively. When the SRP and REMPI beams are subsequently overlapped, a fraction f of the molecules are removed from the ground state and the REMPI signal will be f times weaker. In the case of the SF study, the REMPI signal was measured with the Stokes beam of the SRP lasers tuned to and away from the line center of the transition. The signal was reduced by a factor of 2 (i.e., $f = 0.5$) with the Stokes beam on resonance, and was unchanged with the Stokes beam off resonance. This result was interpreted to indicate that the SRP process was saturated, that is, nearly 50% of the population in the N_2 ($v = 0, j = 6$) level had been transferred to the N_2 ($v' = 1$, $j' = 6$) level for subsequent scattering experiments. The KAZ study also reported that the $Q_{10}(1)$ transition for H_2 was saturated, but instead performed the measurement with both the pump and Stokes beams physically blocked or unblocked. As part of our continuing effort to understand the H + H_2 scattering system in greater detail, we tried to reproduce the saturation result of KAZ with the $Q_{10}(1)$ SRP line of H_2. We found that under certain conditions the measurement is drastically obscured by a Stark shift in the REMPI transition,[23] leading to a false estimate of the quantity f. This Stark shift originates from the intense laser fields of the pulsed pump and Stokes beams present in the focal volume. We describe here in more detail these findings so that other groups may be aware of this effect and avoid this experimental pitfall. On the positive side, under certain circumstances, the optical Stark shift might be used to provide an $|m_j|$-state selector for reaction products, as has been proposed earlier by Zacharias and co-workers.[12]

The experimental conditions were chosen to closely mimic those of the previous study by KAZ, which described

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the gas source (supersonic molecular beam), gas pressure, and focusing conditions of the REMPI and SRP lasers. The instrument used in the current study is also very similar to the one previously used. In our study the laser powers for the pump and Stokes beams exceeded that of KAZ and could be made as high as 100 mJ/pulse and 50 mJ/pulse, respectively. We therefore expected to easily saturate the $Q_{10}(1)$ transition of H_2.

Our first attempt to estimate the fraction of H_2 molecules pumped by SRP was a simple laser power study. First, our REMPI laser was tuned to ionize H_2 ($v' = 1, j' = 1$), which is present in such a small amount that our instrument cannot detect it out of either a gas leak source or a molecular beam. However, a H_2^+ ion signal is measurable when the SRP and REMPI beams are overlapped spatially, indicating that H_2 ($v' = 1, j' = 1$) has been prepared. The SRP laser pulses were delayed roughly 20–30 ns before the REMPI pulse. It is important to note that while the two SRP beams must be overlapped both in space and in time, they need not coincide in time with the REMPI laser as the vibrational lifetimes are much longer than the REMPI process. The overlap of the lasers and their wavelengths are then tuned to their best positions by optimizing the magnitude of this REMPI signal. Figure 1(a) displays the dependence of the signal on the SRP laser power (only the pump beam power is shown, but the Stokes beam power was confirmed to be linear with the pump beam over this range). The power of the REMPI beam is maintained constant during the measurement. The slope of 2.1 in the log-log plot (Fig. 1(b)) is consistent with the two-photon SRP process, and furthermore the form of the curve suggests that the $H_2(v = 0, j = 1) \rightarrow H_2(v' = 1, j' = 1)$ transition is not saturated: we would expect in the saturation region of the curve for the signal to level off with increasing SRP laser power.

Although this measurement suggested that the transition was not saturated, without a full saturation curve, we cannot quantify the fraction of H_2 molecules pumped by SRP. We attempted to measure the fraction f pumped using the method of KAZ. Our REMPI laser was tuned to the center of the $Q(1)$ line of the (0,0) band of the of $E,F\ ^1\Sigma_g^+$–$X\ ^1\Sigma_g^+$ transition. This produced a signal for the initial state of the SRP transition, H_2 ($v = 0, j = 1$). In contrast to our first method, when we overlapped the SRP and REMPI laser beams we found a depletion of the signal. In our initial attempt, the SRP laser pulses again arrived in the chamber 20–30 ns before those of the REMPI. We found that we could not pump more than ~5% of H_2 ($v = 0, j = 1$) into the H_2 ($v' = 1, j' = 1$) state under these conditions. That is to say, we could not discern much difference in the measurement with and without the SRP lasers over the fluctuations of our signal. Figure 4 of Ref. 6 displays an oscilloscope trace of the H_2 ($v = 0, j = 1$) REMPI signal with and without the presence of the SRP beams. The signal appears to be half as large in the presence of the SRP beams implying that 50% of the H_2 ($v = 0, j = 1$) molecules were being pumped into the H_2 ($v' = 1, j' = 1$) state. The reconciliation between our results and those of KAZ comes after consideration of the well-known ac Stark shift.[24]

A typical laser pulse of 6 ns with a Gaussian profile having a 75 μm beam waist and an energy of 100 mJ/pulse has an intensity of 95 GW/cm^2, which corresponds to a peak electric field at the center of the beam profile of 1.2×10^7 V/cm. At such a powerful electric field, the initial, intermediate, and final states of a multiphoton molecular transition undergo Stark shifts arising from the polarizability of the molecule in a given electronic state. Moreover, each $|m_j|$ state has its own energy, that is, the transition also shows Stark splittings. Specifically, for a linear rigid rotor,[25]

$$\Delta E = \frac{I}{2c}\left(\Delta\alpha - \frac{2}{3}\Delta\gamma\frac{3m_j^2 - j(j+1)}{(2j-1)(2j+3)}\right), \quad (1)$$

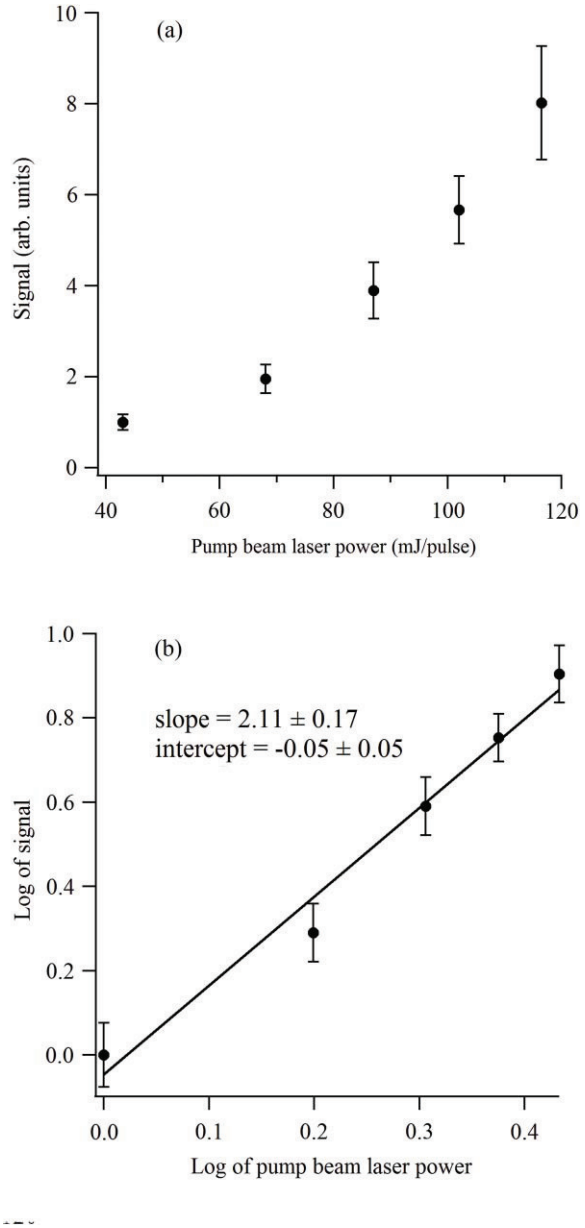

FIG. 1. (a) Integrated H_2 ($v' = 1, j' = 1$) signal as detected using [2+1] REMPI as a function of 532 nm pump beam power, and (b) log–log plot of the same data showing consistency with a two-photon process. For each measurement integrated H_2 ($v' = 1, j' = 1$), signals were obtained for at least 2000 laser shots at each laser power studied, and the error bars shown are calculated as the 1σ uncertainty of these data points. Multiple repeated data sets were collected over several days and were found to be similar.

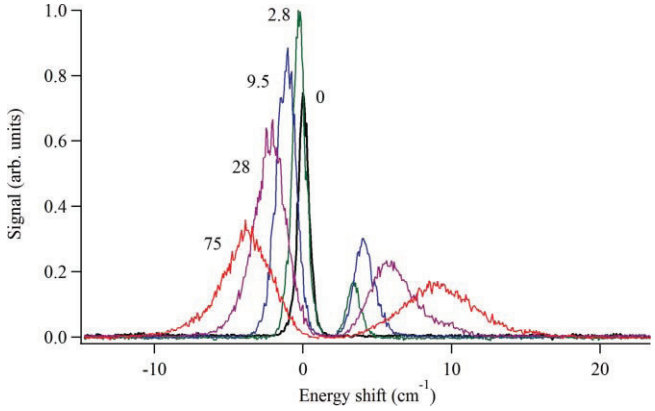

FIG. 2. H_2 ($v = 0, j = 1$) REMPI spectrum at various 532 nm laser intensities (in units of GW/cm^2, displayed in figure). Two effects are at work: (1) the appearance of the blue-shifted second peak arising from the well-known Autler-Townes effect, and (2) the gradual shift of each peak with increasing electric field intensity. Individual $|m_j|$ states are not resolved.

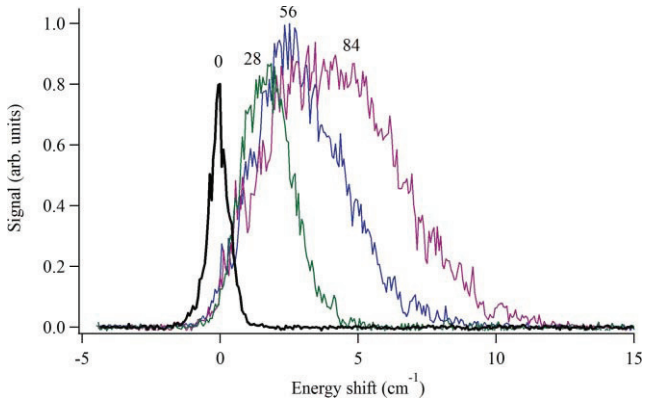

FIG. 3. H_2 ($v = 0, j = 0$) REMPI spectrum at various 532 nm laser intensities (in units of GW/cm^2, displayed in figure). Notice an asymmetric peak broadening that is similar to that observed for the $Q(1)$ line (Fig. 2). Thus, asymmetric broadening rather than shifts and splittings in the $|m_j|$ sublevels mainly contributes to the line profile. The asymmetric broadening in the spectrum of H_2 ($v = 0, j = 1$) arises from an ac Stark shift of virtual levels involved in the REMPI detection scheme as well as any spatial and temporal inhomogeneities in the laser beams.

where I is the intensity of the Stark field, c is the speed of light, and $\Delta\alpha$ and $\Delta\gamma$ are the wavelength-dependent dynamic isotropic and anisotropic polarizability differences between the final and initial states, respectively. Indeed, we found that if the SRP and REMPI beams were temporally overlapped, a shift in both the $Q(1)$ and $Q(0)$ REMPI lines was clearly observed, as shown in Figs. 2 and 3. Consistent with the ac Stark shift, only one of the two pulsed SRP beams was needed to shift each line. From this data it is easy to understand how the shift in the REMPI line in the presence of the nonresonant laser field could easily be mistaken for a real transfer of population out of the ground state by SRP. Measurements of f are typically performed only at the line center of the REMPI transition; the ac Stark shift could go unnoticed without scanning the wavelength of the REMPI laser. Our findings have encouraged us to suggest to those attempting to quantify SRP efficiencies using similar methods to be cautious of this phenomenon, which can lead to false estimates of the value of f. The ac Stark effect is however easily avoided by keeping the SRP and REMPI beams fully temporally separated. We also note that there are other schemes for estimating f.[26]

Comparing Figs. 2 to 3 causes us to conclude that the Stark shift for the particular REMPI scheme we employ to detect H_2 masks the Stark splitting from the two different $|m_j|$ states of $j = 1$. On the contrary, when Raman detection is used, the Stark splittings in the H_2 ($v = 1, j = 1$) state are clearly resolved, as shown in Fig. 5 of Ref. 27. The asymmetric line profile has been observed previously in other REMPI processes, and an explanation for this behavior has been offered in Ref. 23.

Figure 2 displays the H_2 $Q(1)$ REMPI spectrum as a function of the intensity of a nonresonant laser field, the 532 nm pump beam of the SRP process. The $Q(1)$ line splitting is a consequence of the Autler-Townes effect,[28] also known as the dynamic Stark shift or the light shift which has been well documented.[29]

Although the ac Stark effect is often thought of as a complicating factor in many contexts, we also believe, as others before us,[12] that it can be beneficially used to selectively detect molecules from specific $|m_j|$ rotational sublevels. One way to take advantage of the Stark splitting may be to use laser-induced fluorescence as a detection scheme. This approach would avoid intermediate virtual levels, which are subject to Stark shifts in the multiphoton ionization process.

We believe that we have resolved the apparent disagreement between the observation of saturation by KAZ and our current data. The Stark-shifted REMPI lines can be easily mistaken for the saturation in the SRP step. In general, quantitative estimates of any pumping process that employs high intensity electric fields should be calculated only after taking into account the optical Stark effect.

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