Magnetic sublevel specific stimulated Raman pumping of molecular H₂

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(Received 21 November 2001; accepted 27 December 2001)

The magnetic sublevel specific preparation of the |X 1Σ⁺, v = 1, J = 1⟩ state of molecular H₂ using stimulated Raman pumping with circularly polarized light to saturate the Q₀(1) transition is reported. The intensities of S branch rotational Raman scattering signals for the v = 0 and v = 1 states combined with their depolarization ratios measured as a function of pumping light polarization provide direct evidence of the m_J selective nature of the pumping process. This Raman method of non-Boltzmann population preparation does not require a permanent dipole moment and is generally applicable to a wide range of systems. © 2002 American Institute of Physics.

[I. INTRODUCTION]

The intensity and linewidth of currently available light sources has greatly eased the large-scale preparation of molecules in selected electronic, vibrational, and rotational states. Accessibility of specific [e,v,J] molecular states enables an extremely sensitive and comprehensive study of molecular interactions, chemical reaction kinetics, and reaction dynamics. Magnetic sublevel specific phenomena, such as those that occur in gas–surface scattering, magnetic resonance spin-lattice relaxation times, and non-Boltzmann nuclear spin populations in simple diatomic molecules following catalytic reactions at low temperature also provide high resolution details about collisional processes. Although there have been several reports of how the magnetic quantum number m_J changes during a collision, the exact mechanism for how m_J changes is not well understood. There has been some debate over the selection rules for a change in m_J during collisional energy transfer in the gas phase and three ideas have been proposed: (i) the m_J quantum number does not change in a collision, resulting in a Δm_J = 0 selection rule, (ii) the spatial orientation of the molecule does not change, giving a Δθ = 0 propensity rule, where θ is a classical angle representing a quantum mechanical property, i.e., cos(θ) = m_J[2(J + 1)]⁻¹/₂, and (iii) the angular momentum is conserved, dictating that |Δm_J| is less than the total angular momentum J. Unfortunately, experimental limitations on m_J specific state preparation have prevented detailed study of these energy transfer mechanisms. A typical study involves optically pumping molecules into high angular momentum molecular excited states, thus populating states with many different m_J values. This approach is chosen primarily because population distributions that are anisotropic in the m_J quantum number can easily be obtained by directly pumping O- or S-branch rotational transitions.

In addition to the collisional preparation of aligned or oriented molecules mentioned above, numerous more active approaches towards partial molecular alignment or orientation, using tools such as a strong electric field, have been employed. Bernstein et al. pioneered the use of a molecular beam apparatus that aligns polar molecules with an electrostatic hexapole field. While orientation and alignment selects molecular states of well-defined angular momentum, the electric field methods are not applicable to molecules lacking permanent electric dipole moments or those with isotropic or small anisotropic molecular polarizabilities. Extremely high electric field values applied via laser excitation mixes magnetic sublevels, but as shown by Rudert et al. lower practically accessible field amplitudes simply shift the energy levels. Another way of populating states with well-defined angular momentum characteristics in molecules without permanent electric dipole moments involves exploiting the well-defined polarization properties of state of the art pulsed lasers.

A previous paper demonstrated that stimulated Raman pumping can be used to saturate the Q₀(1) transition (Δv = 1, v' = 0, ΔJ = 0, J' = 1) in molecular hydrogen. Control of the polarization properties of the Raman pumping light leads to magnetic sublevel-specific population of the |X 1Σ⁺, v = 1, J = 1⟩ state in H₂. The purpose of this paper is to experimentally illustrate this preparation in H₂ gas by monitoring the intensity and polarization characteristics of the Raman scattering from the |X 1Σ⁺, v = 1, J = 1⟩ state in H₂.

II. POLARIZED RAMAN PUMPING

A detailed analysis of the applied light intensity and polarization dependence of the stimulated Raman pumping process is a necessary first step towards understanding how to prepare a specific |J, m_J⟩ state in a homonuclear diatomic molecule. The effective Hamiltonian that drives the transition from |J, m_J⟩ state to a different |J', m_J'⟩ state is given by

\[ H_{\text{eff}} = \omega_1(J', m_J'; J, m_J) \langle J', m_J' |J', m_J⟩, \]

where the Rabi frequency \( \omega_1(J', m_J'; J, m_J) \) depends upon...
the molecular electric polarizability tensor \( \tilde{\alpha} \) and the intensity and polarization of both stimulated Raman pumping beams \( E^p \) and \( E^D \) in the usual way\(^\text{36} \) as

\[
\omega_{1}(J', m_{j}'; J, m_{j}) = \frac{\sqrt{5}}{4} E^p_{\omega_{p}} E^D_{\omega_{p}} (-1)^{J+m_{j'}} \times \left( \begin{array}{ccc} 1 & 1 & 2 \\ d & -p & p-d \end{array} \right) \times \left( \begin{array}{ccc} J' & 2 & J \\ -m_{j} & d-p & m_{j} \end{array} \right) \langle J' \| \tilde{\alpha} \| J \rangle.
\]

The application of the three-\( J \) symbols and the reduced matrix element in Eq. (2) naturally isolate the angular momentum characteristics of the molecular states and the light polarization from the properties of the electric polarizability tensor \( \tilde{\alpha} \). Equation (2) also presumes that \( \tilde{\alpha} \) is a traceless symmetric second rank tensor—a condition appropriate for a homonuclear diatomiclike molecular \( \text{H}_2 \). Both \( E^p \) and \( E^D \) have well-defined and controllable polarization properties described here by the “photon numbers” \( p \) and \( d \), respectively. Circular polarization corresponds to \( p = 1 \) or \(-1 \), while linear polarization is a combination of these values. Only a nonzero Rabi frequency \( \omega_{1}(J', m_{j}'; J, m_{j}) \) will be capable of driving a transition from the \( |J, m_{j}\rangle \) state to a different \( |J', m_{j}'\rangle \) state, therefore quick analysis of the three-\( J \) symbols in Eq. (2) yields selection rules. When the pumping fields \( E^p \) and \( E^D \) are linearly polarized, the combination of circular helicities indicates that \( m_{j} = m_{j}' \) and \( m_{j} \pm 2 \) in Eq. (2), or \( \Delta m_{j} \neq 0 \pm 2 \). In the case of \( \text{H}_2 \) considered here, saturation of the \( Q_{00}(1) \) transition with linearly polarized light will result in a nearly isotropic population distribution of rotational magnetic \( m_{j} \) sublevels. However, as recognized by Il’inskii et al.,\(^\text{36} \) when the pumping fields \( E^p \) and \( E^D \) are of opposite circular helicity, for example \( p = -1 \) and \( d = +1 \), the product of three-\( J \) symbols in Eq. (2) is only nonzero when \( m_{j} = m_{j}' + 2 \), giving a selection rule of \( \Delta m_{j} = 2 \). In this unique case population transfer will only occur between the \( |v = 0, J = 1, m_{j} = -1 \rangle \) and \( |v = 1, J = 1, m_{j} = +1 \rangle \) state when the \( Q_{00}(1) \) transition is driven by stimulated Raman pumping. For the other combination of circular helicities, \( p = +1 \) and \( d = -1 \), the selection rule is \( \Delta m_{j} = -2 \), resulting in a transition between the \( |v = 0, J = 1, m_{j} = +1 \rangle \) and \( |v = 1, J = 1, m_{j} = -1 \rangle \) state. Since both combinations of circular helicities populate only one \( m_{j} \) level in the exited state, either one may be used to prepare an extremely anisotropic population distribution.

### III. RAMAN DETECTION

The easily resolvable 30.43 cm\(^{-1} \) difference between the \( S_{00}(1) \) and \( S_{11}(1) \) transitions in the \( S \) branch rotational spectrum of a mixture of ground state and vibrationally excited \( \text{H}_2 \) presents one way of measuring the rotational anisotropy in the \( |X^1\Sigma^+ \rangle, v = 1, J = 1 \rangle \) state as shown in Fig. 1. Here the collinear stimulated Raman pumping beams labeled as “pump” and “dump” are counter propagating with respect to a horizontally polarized probe beam. By measuring the intensity of light polarized parallel (\( I_{\|} \)) and perpendicular (\( I_{\bot} \)) to the propagation axis of the probe beam as well as their ratio \( \rho = I_{\|}/I_{\bot} \) for \( S_{11}(1) \) and \( S_{00}(1) \) Raman scattering, the population anisotropy of the \( |v = 1, J = 1 \rangle \) state can be characterized. As shown in a previous study,\(^\text{35} \) saturation of the \( Q_{00}(1) \) transition by stimulated Raman pumping with vertically polarized light generates nearly equal intensity \( S_{00}(1) \) and \( S_{11}(1) \) Raman scattering as shown in Fig. 1(a) for a perpendicular detection geometry. Calculation of the polarizability tensor matrix elements as shown by Long\(^\text{37} \) for the \( S \) branch transitions for vertically polarized light yields a theoretical value for the depolarization ratio of \( \rho = 1 \). Setting the pump and dump beams to have opposite circular helicity as shown in Fig. 1(b) will cause the magnitude of the intensity of the \( S_{11}(1) \) scattering signal to drop by a factor of 1/3. This predicted decrease is simply a reflection of decreasing the population in the \( v = 1 \) state from 1/2 of the unperturbed \( J = 1 \) population in the saturated linear pumping case to 1/6 of the original population for the circular pumping case. Since the population of the \( |v = 0, J = 1 \rangle \) state following circular pumping increases to 5/6 from the 1/2 value during linear pumping, the ratio of the \( S_{11}(1) \) to \( S_{00}(1) \) Raman scattering intensity will drop to 1/5 from the unity value for linear pumping.\(^\text{38} \) Additionally, calculation of the polarizability tensor matrix elements for populations in either the \( m_{j} = 1 \) or \(-1 \) states in \( v = 1, J = 1 \) \( \text{H}_2 \) indicate that for circular pumping the depolarization ratio drops to \( \rho = 0.81 \). Therefore, both a decrease in the ratio of the intensity of \( S_{11}(1) \) to \( S_{00}(1) \) Raman scattering signals from 1 to 1/5 and a decrease in \( \rho \) from 1 to 0.81 demonstrate selective population of either the \( m_{j} = +1 \) or \(-1 \) state in \( v = 1, J = 1 \) \( \text{H}_2 \).

### IV. EXPERIMENT

The experimental apparatus shown in Fig. 2 used to saturate the \( Q_{00}(1) \) transition in \( \text{H}_2 \), and subsequently monitor the rotational \( S \) branch spectrum, is described in detail in a previous publication.\(^\text{35} \) The setup consists mainly of a Spectra Physics model GCR-270 Nd:YAG laser whose frequency
doubled, horizontally polarized 532 nm pumping beam illuminates a Raman shifter pressurized to \( \approx 13.8 \) bar of \( \text{H}_2 \) gas. A \( \lambda > 650 \) nm filter is used to select the output stimulated Raman pumping beams at 683 nm and 954 nm, which are focused into a 7 cm\(^3\)/min stream of \( \text{H}_2 \) at atmospheric pressure. A custom made waveplate (CVI Laser Corporation, #QWPD-683-0.25-954-0.75-10-R15) is used to establish proper polarization of the pumping beams. The frequency tripled \( \approx 0.8 \) mJ/pulse 355 nm light is time delayed and used exclusively for detection of the \( S \) branch transitions in \( \text{H}_2 \) by rotational Raman spectroscopy. A half waveplate is used to control the linear polarization of the probe beam, which is then focused into the \( \text{H}_2 \) stream, overlapping both the 683 nm and 954 nm beams. When routed as shown in Fig. 2, the 355 nm light pulse is time delayed by either 10 ns or 15 ns from the Raman pumping pulses. Rotational \( S \) branch Raman scattering is collected with an \( f/2 \) lens in a direction perpendicular to the propagation axes of the laser beams, as shown in Fig. 1. A polarizing beam splitter is used to select the parallel or perpendicular component of the scattered light for depolarization ratio measurements. Finally, the selected light is directed through a polarization scrambler onto a 900 groove/mm grating housed within a Hilger Watts Monospec 600 monochromator. Signal detection is achieved using a Hamamatsu R-1477 photomultiplier tube and a gated integrator prior to digitization with a Tecmag data acquisition system.

V. RESULTS AND DISCUSSION

The spectrum in Fig. 3 demonstrates the saturation properties and operation of the setup shown in Fig. 2. The peaks centered at 354.37, 587.09, 814.45, and 1034.69 cm\(^{-1}\) are the respective \( S_{00}(0) \), \( S_{00}(1) \), \( S_{00}(2) \), and \( S_{00}(3) \) pure rotational Raman transitions in \( \text{H}_2 \) in the \( v=0 \) state, while the additional signal at 556.66 cm\(^{-1}\) represents the \( S_{11}(1) \) transition in \( \text{H}_2 \). The increase in noise at \( \approx 975 \) cm\(^{-1}\) is due to momentary ignition of the \( \text{H}_2 \) flow. The data in Fig. 4 show just the spectral region around the \( S_{00}(1) \) and \( S_{11}(1) \) transitions with no pumping in (a), linear pumping in (b), and circular pumping in (c). These three spectra were fitted to two Gaussian curves whose areas were compared to obtain population ratios. Difference spectra between the data and fitted curves are also shown below each spectrum in Fig. 4. As expected linear pumping results in roughly equal signal intensities representing an isotropic \( m_J \)-level population distribution in the \( v=1 \) state. However, when pumping beams of opposite circular helicity are used the area of the \( v=1 \) signal centered at 556.66 cm\(^{-1}\) decreases by 76%. This intensity decrease yields a \( S_{11}(1) \) to \( S_{00}(1) \) intensity ratio of 0.24. A summary of the calculated and measured \( S_{11}(1) \) to...
Raman scattering is given in Table I. While the S distribution specified by the Raman preparation with circularization ratios provide a direct measurement of the exact population distribution among magnetic sublevels, the depolarization ratios suggest an anisotropic dependence on the time scale of the experiment. If the collisional depolarization rate exceeds the collision rate potentially mixes the magnetic sublevels in the beam is not a significant effect. At higher pressures, the collisional depopulation of the prepared state in a molecular specific preparation can be accomplished in a simple optical cell requirement of the Raman pumping method, as the state specificity used for molecular beam experiments is not a pressure typically used for molecular beam experiments is not a requirement of the Raman pumping method, as the state specific preparation can be accomplished in a simple optical cell with pressures of one atmosphere or more. At lower pressure, collisional depopulation of the prepared state in a molecular beam is not a significant effect. At higher pressures, the increased collision rate potentially mixes the magnetic sublevels on the time scale of the experiment. This level mixing manifests itself in both the preparation and detection phase of the experiment. If the collisional depolarization rate exceeds the inverse duration of the pulse, here \( \approx 10^8 \text{s}^{-1} \), then a specific angular momentum with respect to the laser beam is difficult, if not impossible, to define. In this high collision limit, there should be no difference between the Raman scattering of linearly versus circularly polarized Raman pumping. Since the experiments surveyed here display a strong dependence on pumping light polarization, it is most likely that magnetic depolarization in \( \text{H}_2 \) is slower than the \( \approx 10 \text{ns} \) long laser pulses. To experimentally verify this contention, both the intensity and depolarization ratios as a function of decreasing pressure could be monitored. However, since pure rotational Raman scattering is not sensitive enough to produce results at low pressures, an alternative detection technique is needed to examine the effects of collisions. One alternative approach is coherent anti-Stokes Raman spectroscopy (CARS), an extremely sensitive nonlinear optical method capable of generating signals from samples of only a few Torr.\(^{39}\) In addition to short time effects, collisional depolarization can also modify the measured Raman scattering intensity and polarization as a function of time between the pump/dump preparation pulses and the 355 nm probe pulse. The timing of the laser pulses in Fig. 2 was chosen such that the time delay between the maximum of the pump/dump pulses and the probe pulse was 10 ns. Again, given that the measured depolarization ratios and that the Raman scattering intensity are close to the anticipated theoretical values, collisional magnetic depolarization is not important on the 10 ns time scale, consistent with the previous discussion. An additional experiment where the pump/dump-probe light pulse delay was increased to 15 ns yields intensity and depolarization ratios similar to the values quoted in Table I, again suggesting that collisional magnetic depolarization occurs on a much longer time scale. It is clear from this discussion that further experiments involving longer delay times between preparation and probe light pulses are warranted. Indeed, an additional frequency tripled Nd:YAG laser is currently being interfaced with the system shown in Fig. 2 to access time delays up to 10 \( \mu \text{s} \) and the results of these planned experiments will be presented in a separate publication.

Finally, it is important to note that while numerous methods have been shown to populate specific rovibrational states,\(^{35,39,40}\) or a band of magnetic sublevels,\(^{20}\) the use of circularly polarized light is the only method that enables population of individual magnetic sublevels. Rudert \textit{et al.}\(^{34}\) used this technique to selectively populate individual levels and a band of magnetic sublevels in high-energy molecular electronic states. However, their use of laser induced fluorescence with circularly or linearly polarized light as a detection method introduced some ambiguity into their experiment due to the change in polarization of the probe beam. While the use of an electrostatic hexapole field by Bernstein \textit{et al.}\(^{29–31}\) proved successful for obtaining well-defined angular momentum states, the alignment method is only valid for molecules with permanent dipole moments. Stimulated Raman pumping with circularly polarized light is possible for molecules lacking a permanent dipole moment, in addition to those possessing one, thus allowing examination of fundamentally important homonuclear and heteronuclear diatomics such as HD, D\(_2\), N\(_2\), and F\(_2\). In fact, this method can be generalized to any molecule with Raman active vibrational bands. The combination of polarization selection with high resolution Raman pumping allows one to consider the preparation of \( J, K \), and \( m_J \) specific levels in both diatomic and polyatomic molecules.

### Table I. Comparison between experimental and theoretical values for the \( S_{11}(1) \) and \( S_{00}(1) \) Raman scattering intensity ratio and depolarization ratio for different applied light polarizations.

<table>
<thead>
<tr>
<th>Light polarization</th>
<th>( S_{11}(1)/S_{00}(1) ) Intensity ratio</th>
<th>Depolarization ratio</th>
<th>Theory</th>
<th>Experiment</th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>1</td>
<td>1</td>
<td>0.974 ( \pm 0.041 )</td>
<td>0.974 ( \pm 0.041 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Right circular</td>
<td>0.20</td>
<td>0.24</td>
<td>0.81</td>
<td>0.81 ( \pm 0.048 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Left circular</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Reference 37.
VI. CONCLUSIONS

The population of specific $|\nu, J, m_J\rangle$ quantum states in molecular hydrogen is possible using stimulated Raman pumping with careful control of circularly polarized light. Based on the theoretical analysis presented above, the Raman pumping method can be extended not only to HD and $D_2$, but to other important molecular systems as well. The ability to prepare specific quantum states in excited vibrational levels will enable experimental investigations of quantum level specific reaction dynamics and collisional energy transfer. Studies examining the loss of the prepared magnetic anisotropy as a function of time, pressure, and temperature are currently in progress. Examination of energy transfer from a well-prepared quantum state in $H_2$ and $D_2$ will provide an excellent opportunity for comparison of theoretical collision dynamics with experimental observations. Finally, it is anticipated that CARS detection will prove to be a more sensitive probe of the anisotropic magnetic sublevel preparation than the rotational Raman scattering used in the current study.

ACKNOWLEDGMENTS

One of the authors (M.P.A.) gratefully acknowledges the National Science Foundation under Grant No. CHE-9504655 for support during the course of this work. The author P.B.K. thanks the NIEHS Superfund Basic Research Program (Grant No. 3-P42-ES04699). The author M.P.A. is a David and Lucile Packard Foundation and Alfred P. Sloan Foundation fellow.