

Establishment of a Molecular-Vibration Decay Route in a Liquid

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The decay route of the methyl vibrations in ethanol excited by stimulated Raman scattering is shown to be a splitting into daughter vibrations of half the frequency. Measurements of the growth and the decay of these daughter vibrations are reported for the first time using picosecond probe techniques.

Because of the rapid decay of molecular vibrations in liquids and of optical phonons in crystals the temporal dynamics of the decay processes have received little attention. With the introduction of laser-probe techniques,¹ in particular in the picosecond time domain,^{2,3} the decay times of optical phonons and molecular vibrations were established for the first time.^{2,3} In this Letter we report the first observation of a *decay route* of a molecular vibration in a liquid and the growth and decay of subsidiary vibrations. The methyl vibrations⁴ at $\sim 2928\text{ cm}^{-1}$ in ethanol ($\text{C}_2\text{H}_5\text{OH}$) are excited by stimulated Raman scattering⁵ (SRS) with high-power picosecond laser pulses. It is shown by spontaneous Raman scattering with a weak picosecond laser beam that these vibrations decay into vibrations centered⁶ at $\sim 1464 \pm 50\text{ cm}^{-1}$. The intensity of the spontaneous anti-Stokes Raman scattering with the weak picosecond laser beam from the 1464-cm^{-1} vibration as a function of delay time is interpreted as the buildup and decay of the molecular vibrations at $\sim 1464\text{ cm}^{-1}$.

The experimental arrangement shown in Fig. 1

has been discussed previously² and has been altered to detect Raman-scattered light at 90° to the exciting beam.³ The $1.06\text{-}\mu\text{m}$ beam creates molecular vibrations at 2928 cm^{-1} via stimulated Raman scattering in ethanol in a cell of length 3.8 cm . The number of molecular vibrations created at 2928 cm^{-1} is monitored with a gold-doped germanium detector by measuring the stimulated Stokes light at $\sim 1.54\text{ }\mu\text{m}$. A weak $0.5305\text{-}\mu\text{m}$ beam ($18\,850\text{ cm}^{-1}$) is optically delayed relative to the $1.061\text{-}\mu\text{m}$ beam (9425 cm^{-1}) and is used to probe the molecular vibrations present. The spontaneous anti-Stokes Raman light from the same sample region close to the exit face of the cell is observed at 90° scattering angles. The light at 4592 \AA (monitoring the 2928-cm^{-1} vibrations) and at 4923 \AA (monitoring the 1464-cm^{-1} vibrations) is collected by lenses into two spectrometers ($\frac{1}{2}\text{-m}$ Jarrell Ash with RCA 7265 photomultipliers, resolution 30 \AA). The spectrometers are oriented at $+90^\circ$ and -90° with respect to the direction of the probe laser pulses. The spectral width of anti-Stokes Raman light is measured

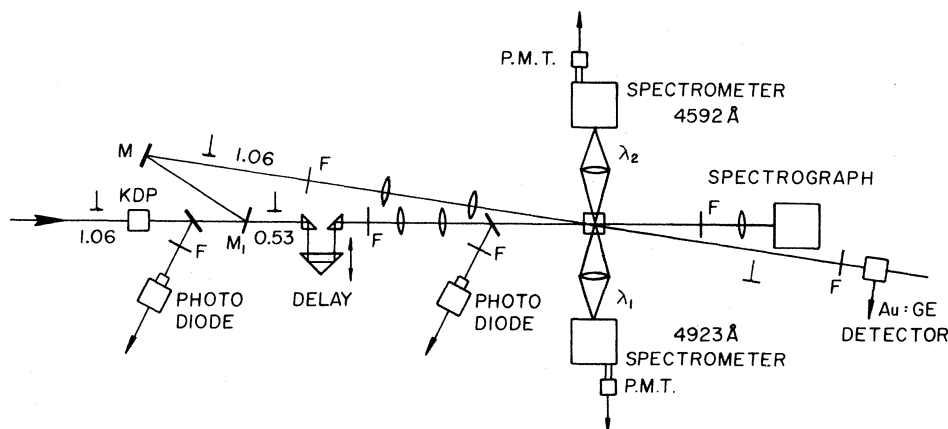


FIG. 1. Schematic of the experimental system.

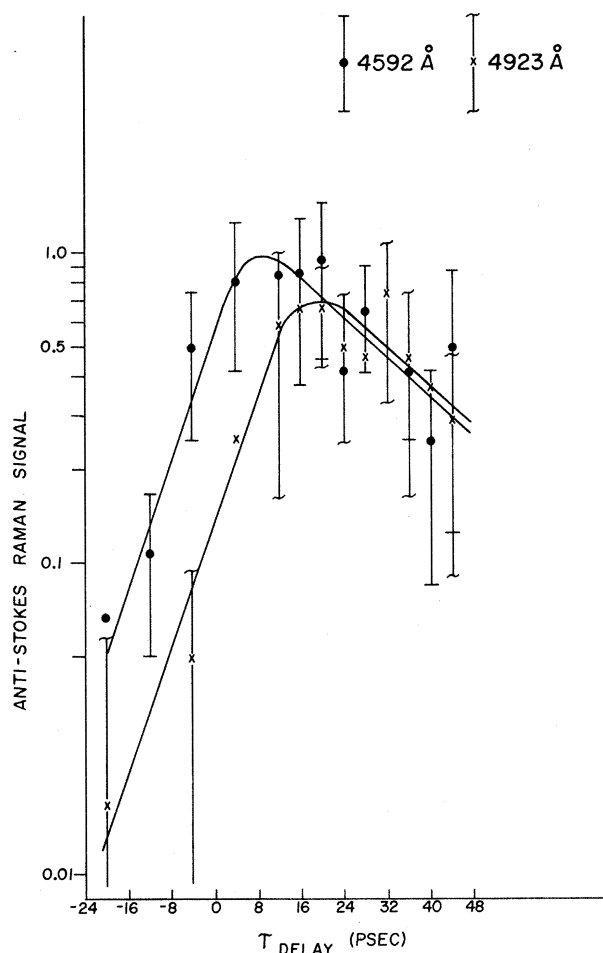


FIG. 2. Normalized anti-Stokes probe Raman signals delay time between the pump and probe laser pulses depicting the growth and decay of the 2928-cm^{-1} vibrations (closed circles) and 1464-cm^{-1} vibrations (crosses) in ethanol. The exponential decay time of the tail is $\sim 28 \pm 14$ psec for both vibrational frequencies.

with an accuracy of $\sim 100\text{ cm}^{-1}$. The signals at 4592 , 4923 , 5305 , and 15400 \AA are then monitored simultaneously with a dual-beam Tektronix 556 oscilloscope with appropriate delay cables. By varying the optical delay of the probe pulse at $0.53\text{ }\mu\text{m}$ relative to the $1.06\text{-}\mu\text{m}$ beam and taking photographs of the four signals at the different delays, the rise and fall of the subsidiary daughter vibrations arising from the 2928-cm^{-1} vibrations is demonstrated. There were no detectable signals on the anti-Stokes side at any other wavelength from 4000 to 5000 \AA above the background level. The signal-to-noise ratio was approximately 4 to 1. No anti-Stokes scattering signals were observed when either the probe or pump beams were blocked. Stimulated Raman light was not

observed at $\sim 1.25\text{ }\mu\text{m}$.

The normalized spontaneous probe Raman light intensity detected at the anti-Stokes wavelengths of 4592 (2928-cm^{-1} shift) and 4923 \AA (1464-cm^{-1} shift) are plotted as functions of delay time in Fig. 2. The rise and decay of the 2928-cm^{-1} shifted probe anti-Stokes intensity represents the rise and decay of the molecular vibration created directly by stimulated Raman scattering, while the rise and decay of the spontaneous probe anti-Stokes Raman scattering at 1464 cm^{-1} is directly related to daughter vibrations originating from the creation of new vibrations from the 2928-cm^{-1} vibrations. The curves are similar to each other except that the 1464-cm^{-1} curve rises later than the 2928-cm^{-1} curve by ~ 10 psec. The normalized intensities of the two curves are comparable within experimental error. The curves are corrected for the photomultiplier tube sensitivities, filter transmission, spectrometer effects, etc.

The detection of light at 4923 \AA established that there is a decay route to vibrations of about half the frequency. The high intensity of the 4923-\AA light strongly suggests that this may be the major decay route of the 2928-cm^{-1} methyl vibrations.⁷ The vibrational frequencies of an ethanol molecule are listed in Table I.⁷ The decay (depopulation time⁸) of 2928-cm^{-1} vibrations appears to be longer than that measured by Laubereau, von der Linde, and Kaiser³; however, their result is within our experimental error. The decay curve of the 1464-cm^{-1} vibrations would appear to indicate a lifetime for the 1464-cm^{-1} vibrations of approximately the same or less than the 2928-cm^{-1} vibrational lifetime. It is, however, difficult to be definitive on the lifetime of the 1464-cm^{-1} vibration because of the possibility of observing the difference frequency between the 2928-cm^{-1} and 1464-cm^{-1} vibrational levels as well as the direct scattering off the 1464-cm^{-1} vibration. The intensity of such a difference-frequency process would follow the decay of the 2928-cm^{-1} vibration to the 1464-cm^{-1} level rather than the decay of the 1464-cm^{-1} level to lower states. The peak anti-Stokes probe Raman intensity at 1464 cm^{-1} relative to the intensity at 2928 cm^{-1} is estimated using the appropriate rate equations for the vibrational levels and is compared with the measured peak ratio intensity (~ 0.7) and delay time (~ 10 psec).⁹ It would appear from this calculation⁹ that both the difference frequency and direct processes mentioned above may be operative, and also that the decay might be both intermolecular and intramolecular.

TABLE I. Vibrational frequencies of ethanol in the notation of Bolla, where the numbers in parentheses beside each frequency are the relative Raman intensities as measured by Bolla with a Hg-arc source, and where the numbers in square brackets are the relative intensities measured with an argon laser with a resolution of 10 cm^{-1} .

$\nu_1 = 256.6 \text{ cm}^{-1}$	(2)		$\nu_{10} = 2878.9 \text{ cm}^{-1}$	(59)	[64]
$\nu_2 = 432.7$	(6)	[11.4]	$\nu_{11} = 2928.8$	(100)	[100]
$\nu_3 = 814.2$	(3)		$\nu_{12} = 2972.5$	(61)	[37]
$\nu_4 = 883.4$	(60)	[78.5]	$\nu_{13} = 3240.3$	(3)	
$\nu_5 = 1051.1$	(32)	[19.5]	$\nu_{14} = 3359.3$	(10)	
$\nu_6 = 1095.8$	(27)	[24]	$\nu_1^* = 1484.3$	(10)	[10.5]
$\nu_7 = 1273.8$	(17)	[9]	$\nu_2^* = 2717.4$	(7)	
$\nu_8 = 1454.8$	(46)	[25.4]	$\nu_3^* = 3632.0$	(2)	
$\nu_9 = 1617.8$	(4)				

The application of this powerful technique for determining decay routes should result in a greater understanding of the nature of rapid structural transformations within media, and should provide insight into the mechanisms behind molecular energy transformation in liquids and solids. In particular the technique should yield detailed information on the vibrational energy transfer rates within and between molecules in pure and mixed liquids.

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¹J. A. Giordmaine and W. Kaiser, *Phys. Rev.* **144**, 676 (1966); F. De Martini and J. Ducuing, *Phys. Rev. Lett.* **17**, 117 (1966).

²R. R. Alfano, *Bull. Amer. Phys. Soc.* **15**, 1324 (1970); R. R. Alfano and S. L. Shapiro, *Bull. Amer. Phys. Soc.* **16**, 53 (1971), and *Phys. Rev.* **26**, 1247 (1971), and in *Phonons*, edited by M. A. Nusimovici (Flammarion, Paris, France, 1971), p. 190. The experimental measured pulse width and spectral width of the exciting $1.061\text{-}\mu\text{m}$ beam are 6 psec and $\sim 80 \text{ cm}^{-1}$, respectively, and of the probe $0.531\text{-}\mu\text{m}$ beam are 4 psec and $\sim 100 \text{ cm}^{-1}$, respectively.

³D. von der Linde, A. Laubereau, and W. Kaiser, *Phys. Rev. Lett.* **26**, 954 (1971); A. Laubereau, D. von der Linde, and W. Kaiser, *Phys. Rev. Lett.* **28**, 1162

(1971).

⁴G. Herzberg, *Molecular Spectra and Molecular Structure: II Infrared and Raman Spectra* (Van Nostrand, Princeton, N. J., 1945).

⁵However, it is possible to excite both ν_2 (CH) and $2\nu_6^{11}$ (CH_3) vibrations (in the notation of Ref. 4) by stimulated Raman scattering as in the case of R. L. Carman, M. E. Mack, F. Shimuzu, and N. Bloembergen, *Phys. Rev. Lett.* **23**, 1327 (1969).

⁶The spectral width of the spontaneous anti-Stokes Raman light shifted by $\sim 1464 \text{ cm}^{-1}$ is $\sim 100 \text{ cm}^{-1}$ and results from the frequency width of the laser, the finite resolution of the spectrometer, and also as a consequence of the SRS dynamical process and finite vibrational lifetime. Vibrational modes located within this 100-cm^{-1} spectral region centered about 1464 cm^{-1} are the 1454-cm^{-1} methyl vibration (ν_8) and 1484-cm^{-1} hydrogen angle variation mode (ν_1^*) (see Ref. 7). If the created vibrations at 2928 cm^{-1} decay via two-quantum decay processes, then the eligible processes must be constricted to $2\nu_8$, $2\nu_1^*$, and $\nu_1^* + \nu_8$ since these vibrational energy quanta sum to $\sim 2928 \text{ cm}^{-1}$, and because of the constraints imposed by the detection of an anti-Stokes signal shifted by $\sim 1464 \text{ cm}^{-1}$. Furthermore, of the three eligible decay routes the dominant route is likely to be $2\nu_8$ since ν_8 corresponds to a methyl vibrational level which is the most intense line in the spontaneous Raman spectra within the 100-cm^{-1} spectral band centered about 1464 cm^{-1} . [The spontaneous Raman intensity at 1454 cm^{-1} (ν_8) is ~ 2.5 times larger than the intensity at 1484 cm^{-1} (ν_1^*)].

⁷The vibrational frequencies of the ethanol ($\text{C}_2\text{H}_5\text{OH}$) molecule are listed in V. G. Bolla, *Z. Phys.* **90**, 607 (1934); S. C. Schumann and J. G. Aston, *J. Chem. Phys.* **6**, 480 (1938); K. W. F. Kohlraush, *Der-Smekal-Raman*

Effect, Ergänzungsband, 1931–1937 (Springer, Berlin, 1938). From Table I one readily finds that the combinations of vibrational levels which add to the methyl (ν_{11}) 2928-cm⁻¹ frequency within a bandwidth of ~ 100 cm⁻¹ (besides the previously mentioned processes $2\nu_8 = 2910$ cm⁻¹, $2\nu_1^* = 2968$ cm⁻¹, and $\nu_1^* + \nu_8 = 2939$ cm⁻¹) are the three-quantum processes $\nu_8 + \nu_5 + \nu_2 = 2938$ cm⁻¹, and $\nu_7 + 2\nu_3 = 2902$ cm⁻¹, where ν_8 is the CH₃ internal vibration, ν_1^* , ν_5 , and ν_3 are the hydrogen angle variation modes, ν_2 is C-C-O skeleton vibration, and ν_7 is a CH₂ internal vibrational mode. Therefore, besides the ν_8 and ν_1^* levels, the 2928-cm⁻¹ mode might also decay to the vibrational levels ν_2 , ν_3 , ν_5 , and ν_7 . However, the latter four levels are reached via three-quantum processes which are usually less probable than two-quantum processes of the type $2\nu_8$, $2\nu_1^*$, and $\nu_1^* + \nu_8$, and are therefore more difficult to detect.

⁸Recently, the dephasing time and depopulation times have been measured using picosecond probe Raman techniques (Ref. 3). When the probe beam is applied at an angle of incidence such that the probe beam, probe Raman intensity, and vibration (created via SRS from the exciting laser) are phase matched together, the measured lifetime is the dephasing time since the probe Raman scattering intensity is sensitive to both the phase and population changes of the molecular vibrations. However, when the probe Raman scattering is detected in a direction in which the phase matching to the created molecular vibration is unimportant, the measured decay time is the depopulation time since the probe Raman intensity is only sensitive to population changes of the molecular vibrations. It has been found (Ref. 3) that $\tau(\text{depopulation}) > \tau(\text{dephasing})$.

⁹The lifetimes of the 2928- and 1454-cm⁻¹ vibrations are $\tau_0 \sim 28$ psec and τ_1 , respectively. To estimate whether the difference-frequency term is operative, the anti-Stokes Raman signal at 1454 cm⁻¹ is defined to be proportional to $\beta_1 n_1(t) + \beta_2 n_2(t)$, and the anti-Stokes Raman signal at 2928 cm⁻¹ is defined to be proportional to $\beta_0 n_2(t)$, where $n_2(t)$ and $n_1(t)$ are the populations of the 2928- and 1454-cm⁻¹ levels, respectively, and the β coefficients denote the spontaneous Raman scattering efficiencies. The term $\beta_1 n_1(t)$ is the contribution due to direct scattering from the 1454-cm⁻¹ vibrational level, the term $\beta_2 n_2(t)$ arises as a result of scattering involving the difference frequency between the 2928- and 1454-cm⁻¹ levels, and the term $\beta_0 n_2(t)$ represents the direct scattering off the 2928-cm⁻¹ vibrational level. From spontaneous Raman scattering data (Ref. 7), the value of β_0 is approximately $2\beta_1$. The value of β_2 in terms of the other β coefficients is not known but can be estimated from the knowledge that the Raman intensity for the combination or difference-frequency process is ~ 0.01 to 1 times the one vibrational quantum process (Ref. 7), and hence $\beta_2 \leq \beta_2$. Taking $\beta_1 = \beta_2$ and $\tau_1 \sim \tau_0/2$, one calculates a delay time of ~ 8 psec between the peaks of the 2928- and 1454-cm⁻¹ anti-Stokes shifted signals and a peak anti-Stokes Raman intensity ratio $I(1454)/I(2928)$ of $\sim \frac{1}{2}$; taking $\beta_1 = \beta_2$ and $\tau_1 \sim \tau_0$, one finds a time of 14 psec between the peak signals and an anti-Stokes Raman intensity ratio of ~ 0.7 . If β_1 is chosen to be substantially greater than β_2 , the calculated Raman intensity ratio does not agree with the experimentally observed value—therefore the suspicion that the difference-frequency process may be playing a role.

Interpretation of an Enhanced Diffusion Observed in a Solid-State Plasma*

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An enhanced Bohm-like diffusion across a magnetic field observed in a germanium plasma near thermal equilibrium can be interpreted in terms of vortex diffusion due to plasma convections which are thermally excited. Both theoretical analysis and numerical simulation show good agreement with the experimental observations.

In this note we show by numerical simulation that an enhanced Bohm-like diffusion observed in a germanium plasma by Gurnee, Hooke, Goldsmith, and Brennan¹ can be interpreted in terms of vortex diffusion due to plasma convective cells.²⁻⁴ These authors found that, for $\omega_{ce}\tau_n > 3.5$ (where ω_{ce} is the electron gyrofrequency, and τ_n is the electron scattering time with the lattice), the diffusion across a magnetic field is more rapid than predicted by collision theory which takes

into account the scattering of particles with the lattice.¹ The observed enhanced diffusion follows more or less a Bohm-like law, $D_{\perp} \propto 1/B$. They confirmed that the enhanced diffusion is reproducible, and they could not detect any enhanced fluctuations though enhanced fluctuations of a few times the thermal level would not be detectable.

We show by numerical simulation in three dimensions that a similar enhanced plasma diffusion can be reproduced for the same parameters