

## Ground State Wavepackets in Pump-Probe Spectroscopy

### Abstract

We discuss the pump-probe signals expected from ground state wavepackets. The concept of a 'pure hole' is examined. The temporal form of the signals can be qualitatively predicted from the pump and probe wavelengths and pulse durations using the classical Franck principle. Temperature is found to play an important role. These considerations are illustrated with quantum mechanical calculations of the iodine ground state transient dichroism signal.

### Introduction

Femtosecond pump pulses typically launch wavepackets on both ground and excited electronic states. Pump-probe spectroscopies [e.g., differential absorption (Pollard and Mathies, 1992), transient dichroism in the diffusive reorientation limit (Scherer et al., 1993)] detect the difference between the probe beam after the sample with and without the pump. This is a combined signal from *both* wavepackets, which must somehow be disentangled. The pump interactions shown in Fig. 1 illustrate how a short, vibrationally abrupt pump pulse excites coherent vibrations on both the ground and excited electronic states. Unfortunately, signals from vibrational wavepackets on the ground vibrational state depend strongly on temperature and the characteristics (e.g. wavelength and pulse duration) of both the pump and probe pulses. In particular, the wavepacket recurrence frequencies need not equal a molecular vibrational frequency.

For simplicity, quantum density matrix treatments of pump-probe signals have usually considered only two vibrational levels in each electronic state (Chesnoy and Mokhtari, 1988; Walmsley et al., 1988), which yields the oversimplified result that cosinusoidal beats are expected at each vibrational frequency difference. Similarly, the importance of temperature does not seem to be widely appreciated. The behaviour for coherent excitation of many vibrational levels is complex and not easily understood by viewing the signals as multi-level quantum beats. Heller and coworkers have emphasized the conceptual and computational advantages of classical mechanics for understanding short time quantum dynamics e.g. wavepacket motion (Heller, 1981) and low resolution spectra

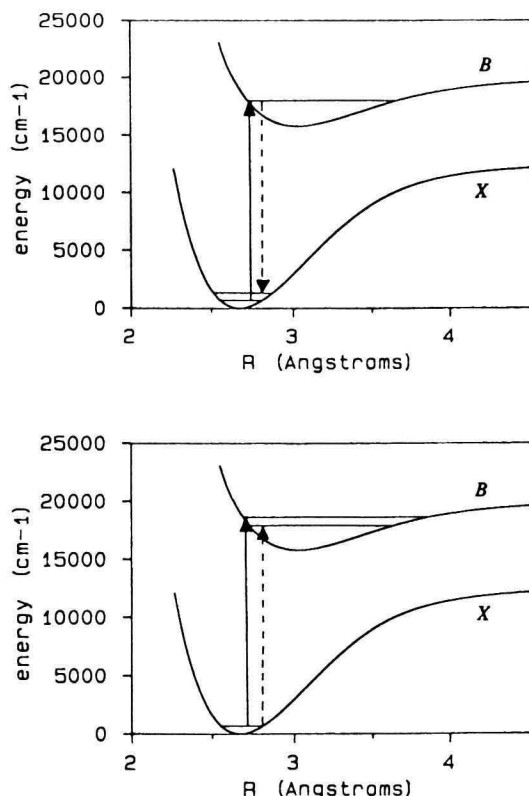


Fig. 1. Illustration of coherent wavepacket preparation on the ground ( $X$ ) and excited ( $B$ ) states of iodine by a 580 nm pump pulse. For this pump wavelength, the outer turning points of the ground state vibrational levels overlap the excited state. Stimulated Raman scattering by the pump excites a coherent superposition of the ground state levels which is initially located near the outer classical turning point of the thermally populated  $X$ -state levels (Fig. 1 (top)). The excited state wavepacket is initially located near the inner classical turning point of the  $B$ -state and is composed of roughly  $v' = 15-19$ , as diagrammed in Fig. 1 (bottom). (Level spacings have been exaggerated for clarity.)

(Reimers et al., 1983; Bergsma et al., 1984). We have found the classical mechanical behaviour of a thermal ensemble is relatively easy to visualize and use to understand pump probe signals. Classical mechanics is only numerically accurate in the high temperature limit,  $\hbar\omega \ll kT$ .

### Classical Wavepacket Dynamics

The classical Franck principle states that nuclei do not have time to move or change velocity during a sudden electronic transition (Franck, 1925). This implies conservation of nuclear kinetic energy during electronic transitions. The classical transition energy is therefore given by the potential energy difference,

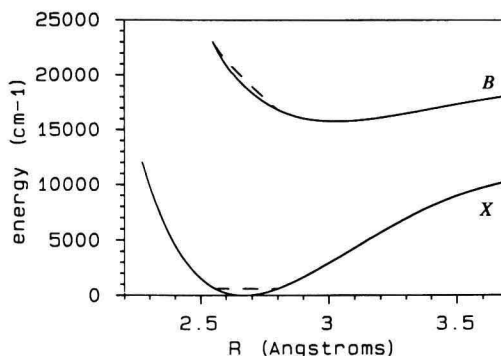


Fig. 2. Mulliken difference potential for  $B \leftarrow X$  absorption by the oscillating wavepacket prepared by the pump pulse. From the classical Franck principle, as the wavepacket passes through a given internuclear distance, absorption occurs at the wavelength which conserves nuclear kinetic energy during the electronic transition. In Fig. 2, the kinetic energy of one trajectory in the ground state wavepacket is superposed (dashed lines) on the  $B$  and  $X$  state potentials (solid lines). For each value of  $R$ , absorption from the  $X$  state can occur classically for photon energies equal to the vertical difference between the two dashed lines (Mulliken difference potential.)

which is a function of the nuclear coordinates. Mulliken difference potentials (Tellinghuisen, 1985) are used to illustrate this point for the  $I_2$   $B \leftarrow X$  transition in Fig. 2. The Franck-Condon principle has sometimes been incorrectly interpreted as implying absorption and emission only from the vicinity of the classical turning points. Note that time averaging, which biases the transition probability towards local extrema of the difference potential in a frequency resolved experiment, is irrelevant for time resolved spectroscopy with pulses fast compared to vibrational motion. In femtosecond experiments, one is quite likely to probe the wavepacket when it has high momentum as it crosses the middle of the well.

Consider an ensemble of classical molecules with energy given by the horizontal dashed line on the potential labelled  $X$  in Fig. 2. A resonant pump pulse which is short compared to half the vibrational period yet spectrally narrow compared to the allowed range of transition energies will only electronically excite those molecules which pass through a small range of internuclear distances during the pump pulse. This launches a group of molecules ('wavepacket') on the excited state and leaves a complementary 'hole' in the ground state ensemble, both of which can modify a subsequent probe pulse.<sup>1</sup> The internuclear distance at which a wavepacket is probed by a given wavelength can be approxima-

<sup>1</sup> Classically, the Fourier transform limit for an electromagnetic wave implies an optimum pulse duration for producing a narrow hole: if the frequency spread is made smaller to excite a smaller range of internuclear distances then the pulse is necessarily longer and molecules travel in and out of the pumped region during the pulse; conversely a shorter pulse has a broader spectrum and excites a larger range of internuclear distances. The optimum pulse duration for a narrow ground state hole is not necessarily the same as that for a narrow wavepacket on the excited state.

tely calculated from the Mulliken difference potential by the classical Franck principle. The absorption frequency at which a particular internuclear distance is probed should not be expected to be accurate to better than a vibrational quantum.

By probing with different wavelengths, we can follow the excited state wavepacket and ground state hole as they move back and forth (Bernstein and Zewail, 1989; Scherer et al., 1993). Consider the wavepacket prepared on the lower electronic state in Fig. 1. Classical mechanics allows one to understand that the ground state wavepacket interacts with a probe pulse as an oscillating 'hole' which is probed each time it passes through the range of internuclear distances dictated by the probe center wavelength. For instance, as one tunes the probe to the blue of the 580 nm pump in Fig. 1, one probes the ground state wavepacket at smaller  $R$ . In the middle of the well, a green probe beam will interact with the hole twice per vibrational period after an initial delay of roughly a quarter vibrational period. At the inner wall, a blue probe will interact with the hole once per vibrational period after an initial delay of about half a vibrational period.

Raman processes in which molecules are transferred to the excited state, move on the excited state potential, and then returned to the ground state by the pump also occur. These non-abrupt processes only occur to the extent that vibrational motion is possible during the pump pulse, but if they are sufficiently rapid and the temperature is low, they can cause excess population at some internuclear distances even though the net population of the ground electronic state has been depleted. The relevant vibrational timescale for these non-abrupt Raman processes depends on the excess kinetic energy acquired in the excited state (determined by the difference potential) before the molecule moves outside the range of internuclear distances sampled by the pump spectrum. Non-abrupt Raman processes are therefore less important for a pump Franck-Condon region near the classical turning point (where molecules move slowly) than a pump Franck-Condon region near the ground state equilibrium geometry.

If  $\rho(R, t)$  is the probability distribution for internuclear distance,  $R$ , in given classical ensemble at time  $t$ , then the absorption cross section is given by [Bergsma et al., (1984) Eq. 2.13]

$$\sigma(\omega) = \frac{4\pi^2\omega}{\hbar c n} \int \mu(\omega : R) \rho(R, t) \mu(R : \omega) dR. \quad (1)$$

We write  $\mu(R : \omega)$  to emphasize that absorption of light with frequency  $\omega$  can only take place when the molecule is at the internuclear distance  $R$  determined by the classical Franck principle. The number of photons absorbed is proportional to

$$A \propto \int \int E(\omega, t) \sigma(\omega) E(\omega, t) d\omega dt \quad (2)$$

Photon detected pump-probe signals,<sup>2</sup>  $S$ , are proportional to  $A - A_{EQ}$ , where  $A_{EQ}$  is the equilibrium probe absorption, and thus depend on  $\delta\rho(t) = \rho(R, t) - \rho_{EQ}(R)$ . For an electronically excited state,  $\delta\rho_e(t)$  is always positive for all  $R$ , since  $\rho_{EQ}$  is zero, i.e. we have a pure wavepacket. Since only the squares of  $\mu$  and  $E$  enter into Eq. (1) and (2), this fixes the sign of each excited state pump-probe signal<sup>3</sup> so that the pump-probe signal never passes through zero. For the ground state,  $\rho_{EQ}$  is not zero and  $\delta\rho_g(t)$  need not be negative for all  $R$ . In this case, the ground state pump-probe signal does not have a definite sign. If non-abrupt Raman processes which require nuclear motion during the pulse can be neglected,  $\delta\rho_g$  is negative [ $\delta\rho_g(0) \approx -\delta\rho_e(0)$ ], i.e. we have a pure hole and the ground state pump-probe signal is signed.

## Quantum Correspondence

It is helpful to view pump-probe signals as periodic absorption and/or emission by oscillating wavepackets on the ground and excited states. The appropriate formulas analogous to Eq. (1) and (2) involve the density matrix,  $\rho$ . The quantum analogue of Eq. (2) is

$$A \propto \frac{4\pi^2\omega}{\hbar c n} \text{Tr}(E\mu\rho\mu^*E^*) \quad (3)$$

(the integrals over  $\omega$  and  $t$  have been suppressed for clarity). The pump probe signal is determined by  $\delta\rho(t) = \rho(t) - \rho_{EQ}$ , where  $\rho(t)$  is the density matrix of the system after interaction with the pump and  $\rho_{EQ}$  is the equilibrium density matrix. For the excited electronic state,  $\delta\rho(t) = \rho_e(t)$ , the vibrational density matrix of the excited state, therefore the excited state pump-probe signal is signed (i.e., cannot pass through zero) by the density matrix inequality  $\xi^*\rho\xi \geq 0$  for an arbitrary vector  $\xi$  (Landau and Lifschitz, 1977). We refer to a coherent state where  $\delta\rho$  is 'positive' as a 'pure particle.'

The ground state pump-probe signal is more complicated. Clearly, coherent vibration on the ground electronic state arises from stimulated Raman scattering. For the ground state, the diagonal elements of  $\delta\rho(t) = \rho_g(t) - \rho_{EQ}$  in the eigenstate basis need not all be negative when Raman processes are considered. For a non-resonant pump pulse, some of the diagonal elements of  $\delta\rho(t)$  are positive and some are negative (ground state population is redistributed but not

<sup>2</sup> Experiments which detect changes in total photon number do not detect stimulated Raman scattering of the probe beam, since this simply exchanges red and blue probe photons without changing the total probe photon number. The experiments discussed by Pollard and Mathies (1992), in which the probe beam is spectrally dispersed, do detect such exchanges between red and blue probe photons and hence are sensitive to stimulated Raman scattering of the probe.

<sup>3</sup> It is sometimes possible to probe more than one electronic transition with a single wavelength. In this case, the pump-probe signal for each electronic transition is signed, but the total signal may not be.

removed) so that  $\delta\rho$  is not 'negative' (Hoffman and Kunze, 1971) and the pump-probe signal can oscillate between positive and negative values. The classical theory suggests that for impulsive resonant excitation,  $\delta\rho_g(0) \approx -\delta\rho_e(0)$ . When  $\delta\rho$  is 'negative,' we have an inequality  $\xi^* \delta\rho \xi \leq 0$  for an arbitrary vector  $\xi$  and refer to the coherent vibrational state as a 'pure hole.' All pump-probe signals from a 'pure hole' are signed, which simplifies the interpretation immensely.<sup>4</sup>

The signal for a pure hole is a quantum beat,<sup>5</sup> e.g.

$$S = Ae^{-t/T_1} + \sum_i B_i \cos(\omega_i t + \phi_i) e^{-t/T_2} \quad (4)$$

where  $A$  and  $B_i$  have the same sign and obey inequalities which may be formally derived from the density matrix inequality given above. Similarly,  $T_1 \geq T_2$  by the density matrix inequality  $|\rho_{ij}| \leq \sqrt{\rho_{ii}\rho_{jj}}$  (Landau and Lifschitz, 1977). The interpretation of any fit to Eq. 4 must assure that the terms attributed to each electronic transition obey the above inequalities.

Whether the coherent vibration on the ground electronic surface approximates a 'pure hole' or not depends on the temperature and the characteristics of the pump. For simplicity, we restrict our discussion to the case where the transition dipole is independent of nuclear coordinates. For a  $\delta$ -function pump pulse, there is no time to move on the excited state potential and we have a uniform depletion of all vibrational levels (Tanimura and Mukamel, 1993). This is a boring pure hole because it doesn't move, but it seems reasonable to expect that shorter pulses will excite coherent vibrations that better approximate a pure hole. For real pulses, in order to have a pure hole, it is necessary to depopulate higher lying levels faster than population is transferred into them from lower levels by resonant impulsive Raman scattering. This should be possible if the Franck-Condon factors increase faster than the Boltzmann factors drop: i.e. Franck-Condon factor times Boltzmann factor increasing with vibrational excitation. This criterion can be approximately met when the vibrational displacement is large, the spectrum at the pump wavelength is dominated by hot bands, and the temperature is sufficiently high relative to the vibrational frequency. These circumstances seem closely related to the classical situation discussed in the last section, but hold only approximately for our example of molecular iodine at room temperature.

## Examples

We shall illustrate the points discussed above with transient dichroism results reported for a solution of iodine in hexane at room temperature by Scherer,

<sup>4</sup> Note that a signed pump-probe signal does not imply the coherent vibration is a pure hole. We have not yet examined the matrix  $\delta\rho$  to determine how accurately the examples shown below approximate pure holes.

<sup>5</sup> Eq. 4 assumes that all vibrational levels have identical population ( $T_1$ ) and coherence ( $T_2$ ) lifetimes.

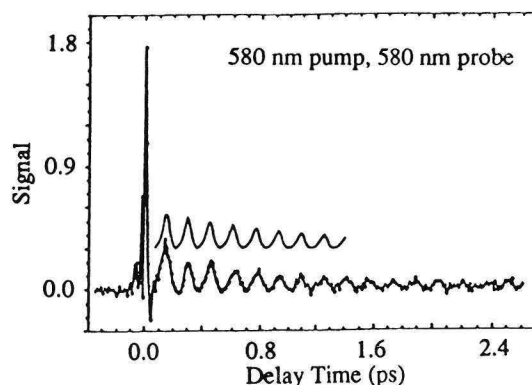


Fig. 3. Calculated ground state pump-probe signal and observed transient dichroism signal for 580/580 pump/probe wavelengths. The observed signal is the sum of a positive transient dichroic response from  $B \leftarrow X$  absorption (analysis recovers a large damped cosine at  $220 \text{ cm}^{-1}$ , a smaller damped cosine at  $420 \text{ cm}^{-1}$ , and a positive 1500 fs exponential decay) and a negative response from absorption by the  $B$ -state wavepacket. The ground state signal is attributed to probing the  $X$ -state wavepacket hole near the outer turning point once per vibrational period, as expected for this probe wavelength from the classical Franck principle and the Mulliken difference potential. The calculated pump-probe signal has been multiplied by a 1200 fs exponential decay and displaced upwards for comparison.

Jonas and Fleming (1993) and new calculations of the ground state pump-probe signal using the gas-phase iodine potentials. The iodine ground state vibrational frequency is  $211 \text{ cm}^{-1}$  (which approximately equals  $kT$  at room temperature) in both hexane and the gas phase. One simplifying aspect of the iodine examples shown here is that the difference potential for  $B \leftarrow X$  absorption (Fig. 2) decreases monotonically with increasing  $R$ . Therefore, each probe wavelength accesses only one value of  $R$ .

The quantum calculations are carried out to demonstrate the correspondence between classical and quantum description of the ground state behavior laid out above. The potential used here are cubic spline interpolated RKR potentials.<sup>6</sup> The first four vibrational eigenstates of the ground potential surface, i.e. those with any significant Boltzmann weight, are found numerically by an algorithm based on the Numerov-Cooley method (Cooley, 1961) with the simplification introduced by Ross (1983). For each ground vibrational eigenstate a propagation is carried out for the ground and excited state wavepackets created by interaction of the iodine molecule with the pump pulse. This coupled calculation, which carries the molecule-field interaction to infinite order in the electric field, is performed by solving the time dependent Schrodinger equation (see for example equation 4.29 of Scherer et al., 1991). The time propagator is approximated by the second order differencing method and the nuclear kinetic energy is eval-

<sup>6</sup> The  $X$ -state potential is from LeRoy (1970). The  $B$ -state potential is from Barrow and Yee (1973) [note the typographical error for  $G(v=46)$  which should read  $G(v) = 3892.86 \text{ cm}^{-1}$ ] and Tellinghuisen (1973).



uated by fast Fourier transform. (Kosloff, 1988) In the calculation the coupling is given by  $\mu E_0 \cos(\omega t) \exp(-t^2/\tau^2)$ . Both pump and probe pulses are chosen to be Gaussian with FWHM of 15 fs and  $\mu E_0 = 0.001$  atomic units; the variation of the electronic transition moment with  $R$  (Koffend et al., 1979) has been neglected.

Stimulated Raman processes lead to motion of the ground state quantum wavepacket. The interaction of the probe pulse with the ground state wavepacket is subsequently calculated, once again by explicit coupled propagation, as a function of pump-probe delay time. Prior to initiating the probe pulse the excited state amplitude is removed, so as to eliminate any interference effects (in contrast to the phase locked pulse pair signal of Scherer et al., 1991). The  $B \leftarrow X$  transition probability, evaluated at the end of the probe pulse, is stored at each delay. From equation (3), the pump-probe signal is evaluated as a difference of the pump attenuated  $B \leftarrow X$  transition probability. The ground state transient dichroism signal (which is the *negative* of the pump-probe signal) is shown in all figures.

The signals due to each initial ground eigenstate are summed after weighting by the appropriate Boltzmann factor. Simulations have been performed for two probe wavelengths with a 580 nm pump. 580 nm probes the outer turning point (see Figure 1) whereas a 526 nm probe wavelength interrogates the ground state wavepacket as it passes through the center of the well (this can be deduced from the Mulliken difference potential in Fig. 2).

The 580 nm pump/580 nm probe (580/580) dichroic signal is shown along with the calculated pump-probe signal in Fig. 3. According to Fig. 2, we expect  $B \leftarrow X$  absorption with zero phase shift at the  $X$ -state vibrational frequency from the outer turning point of the  $X$ -state. This is essentially the observed result,

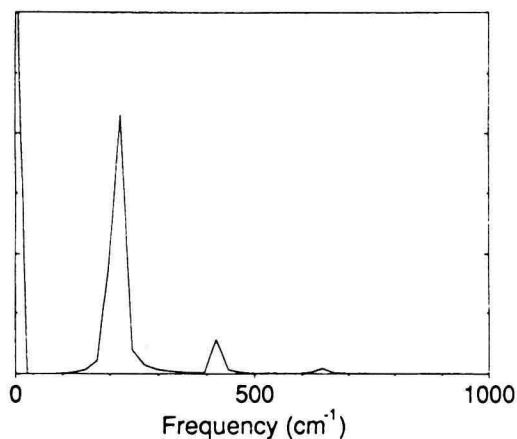


Fig. 4. Fast Fourier Transform (FFT) of the calculated 580/580 pump-probe signal. The first harmonic dominates both the experimental and calculated pump-probe signals, but the second harmonic, which sharpens the peaks, cannot be neglected.



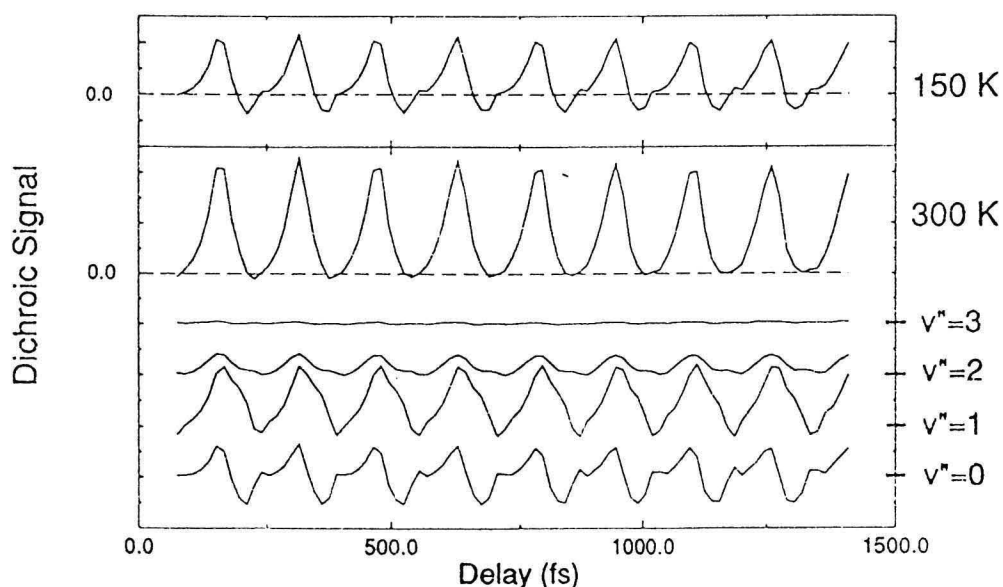


Fig. 5. Effect of temperature and breakdown of the calculated 580/580 pump-probe signal by initial vibrational eigenstates. The top panel shows the signal at  $T = 150$  K, which oscillates through zero (dashed line) and does not have a definite sign. The bottom panel displays the nearly signed signal at  $T = 300$  K and breaks that signal down into contributions from thermally populated initial eigenstates. The signal from each initial state is displaced in the plot, with zero for each trace indicated by the respective tick mark adjacent to the labeled initial vibrational quantum number. Note that the signal for  $T = 0$  K, which would arise entirely from  $v'' = 0$ , is much more complicated than the signed total signal at  $T = 300$  K.

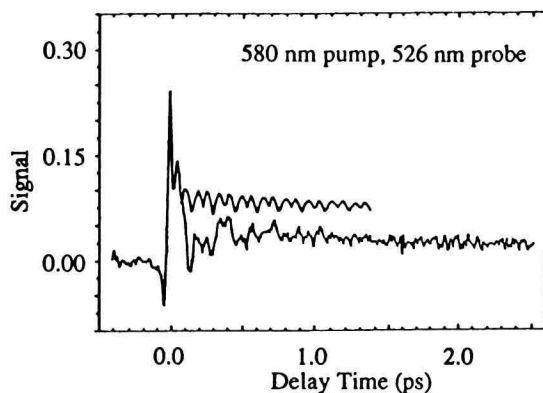


Fig. 6. 580/526 transient dichroic response and calculated ground state pump-probe signal. Analysis of the transient dichroism signal revealed five terms, including a  $423\text{ cm}^{-1}$  damped cosine and a positive exponential. The  $423\text{ cm}^{-1}$  damped cosine and positive exponential have been attributed to probing the  $X$ -state 'hole' as it passes through the center of the well *twice* per vibrational period (hence the doubled frequency). The calculated pump-probe signal has been multiplied by a 1200 fs exponential decay and displaced for comparison (see text).

which also agrees well with our calculations. The Fourier transform of the calculated 580/580 pump-probe signal (Fig. 4) recovers both the fundamental and the second harmonic of the vibrational frequency because the pump-probe peaks are more sharply modulated than a cosine. The second harmonic was also detected in the analysis of the experimental signal.

Fig. 5 illustrates the temperature dependence of the 580/580 signal and displays the signal calculated for each initial vibrational eigenstate. It is clear from Fig. 5 that the concept of a pure hole is useless for a single eigenstate but helpful for a thermal ensemble. Whether the ground state signal is signed or not clearly depends strongly on the temperature.

The 580/526 data is reproduced in Fig. 6. This data set was difficult to interpret, perhaps because the signal to noise is low and analysis recovered five components. From Fig. 2, we expect to probe the wavepacket as it moves across the middle of the *X*-state well. The ground state vibrational coherence signal was experimentally assigned by the  $423\text{ cm}^{-1}$  frequency, (roughly double the ground state vibrational frequency) and the decay time, which is essentially the same as that recovered for the ground state from the 580/580 data. The doubled frequency results from probing the wavepacket as it crosses the middle of the *X*-state potential twice per vibrational period - a result that is borne out by the calculated signal. A comparison between the experimental and calculated signals suggests that the actual time zero occurs about 20 fs after the maximum experimental cross-correlation (not shown) and 40 fs before the maximum electronic response. The calculated pump-probe signal in Fig. 6 has been shifted accordingly. The agreement between experiment and calculation is gratifying. The FFT of the calculated 580/526 pump-probe signal (Fig. 7) shows that the second harmonic of the ground state vibrational frequency is more prominent than the fundamental, as expected from the classical theory. Fig. 8 shows the breakdown of the 580/526 pump-probe signal by eigenstate. The signal is dominated by  $v''=0$ , and thus depends less strongly on temperature than the 580/580 signal. Note the slight asymmetry of the double peaks.

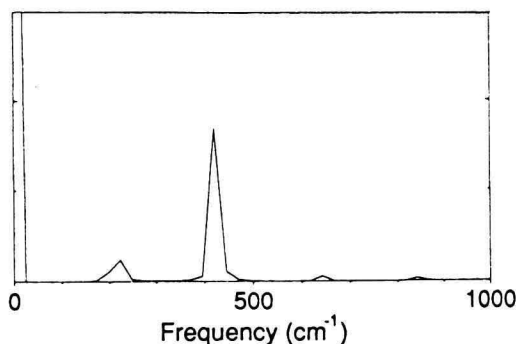


Fig. 7. FFT of the calculated 580/526 pump-probe signal. The second harmonic dominates but there is still some amplitude at the first harmonic.

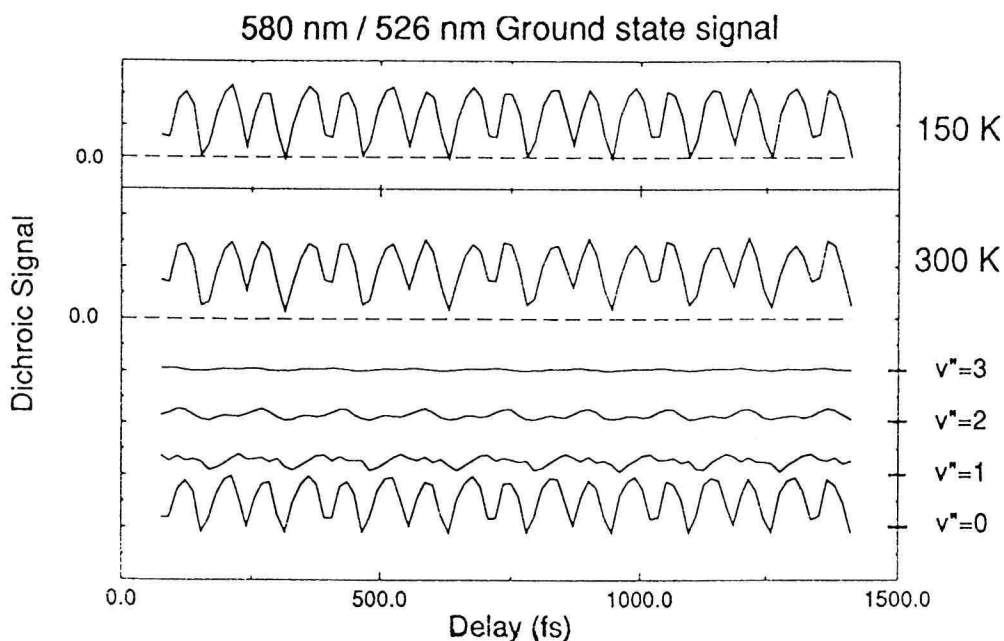


Fig. 8. Breakdown by eigenstates and effect of temperature on the calculated 580/526 pump-probe signal.

## Concluding Remarks

We mention a simple example that illustrates how a ‘hole’ produced by abrupt optical excitation can be viewed as caused by either stimulated Raman scattering or absorption, depending on the states used for calculations. Both viewpoints are equally correct. The model system consists of an electronic ground state with a symmetric double well and an electronically excited state with a single, nearly identical well on the left side only. We take the temperature such that the lowest symmetric,  $|s\rangle$ , and antisymmetric,  $|a\rangle$ , ground vibrational states are essentially equally populated, but all other levels are essentially unpopulated. The density matrix for a system having equal probability to be in either of the localized non-stationary states  $|L\rangle = (|s\rangle + |a\rangle)/\sqrt{2}$  and  $|R\rangle = (|s\rangle - |a\rangle)/\sqrt{2}$  is identical to that for a system having equal probability to be in either of the two eigenstates  $|a\rangle$  and  $|s\rangle$ . It is therefore equally correct to view the system as being in eigenstates or in non-stationary states, since any two systems with the same density matrix are indistinguishable (Von Neumann, 1955).

If we calculate to second order the effect of a short pulse (compared to the inverse tunneling frequency) resonant with the excited electronic state in either set of states, we deplete only  $|L\rangle$  and are left with a coherent ‘hole’ which oscillates back and forth between the two equivalent wells. For the eigenstates, this depletion is calculated as stimulated Raman scattering by  $|a\rangle$  and  $|s\rangle$ , but

the view that this coherent 'hole' arises from absorption of  $|L\rangle$  only is equally correct. If we consider quantum harmonic oscillators at high temperature, randomly phased coherent harmonic oscillator states (Cohen-Tannoudji et al., 1977) are very similar to the classical picture. In the coherent harmonic oscillator basis, the neglect of non-abrupt Raman processes which change  $\langle x \rangle$  or  $\langle p \rangle$  yields a pure hole in the ground state. In the general case, it may be helpful to think of the thermal population on the ground electronic state as distributed over randomly phased coherently vibrating states rather than eigenstates.

A simple classical theory based on the Franck principle is very helpful for gaining an intuitive understanding of the vibrational wavepacket modulation of the individual pump-probe signals, and has been used to qualitatively predict the iodine  $B \leftarrow X$  transient dichroism as a function of probe wavelength. Preliminary calculations indicate that the interpretation of ground state signals with the classical Franck principle is essentially correct. For a qualitative understanding necessary to begin fitting data, it may be advantageous to perform pump-probe experiments in the limit where the ground state wavepacket is a pure hole. In the future, we hope to subtract the calculated ground state contribution to the pump-probe signals, form a model for the excited state signals with the classical Franck principle, and then fit the data quantitatively to reveal finer features of the excited state dynamics. The concept of a ground state 'hole' seems to be very useful for understanding pump probe signals.

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