Femtosecond Wavepacket Spectroscopy: Influence of Temperature, Wavelength, and Pulse Duration

David M. Jonas, Stephen E. Bradforth, Sean A. Passino, and Graham R. Fleming*

Department of Chemistry and James Franck Institute, The University of Chicago, Chicago, Illinois 60637

Received: August 3, 1994; In Final Form: October 11, 1994*

We discuss pump–probe signals from the wavepackets which are simultaneously generated on both the ground and excited electronic states by weak optical pulses shorter than one vibrational period. A classical model of localized ground state bleaching and excited state population of the internuclear geometries where the photon energy matches the electronic energy gap predicts the pump and probe wavelength dependence and pulse duration dependence of the pump–probe signals. The classical signal contains higher harmonics of the fundamental vibrational frequency: in particular, if the wavepacket is probed near the middle of the well, the signal is dominated by the second harmonic of the vibrational frequency. We show that all pump–probe signals can be calculated from $\delta g$, the pump-induced change of the density operator, and present both quantum and classical pictures of the change in the ground state vibrational density operator, $\delta g_q$. Computations of the iodine ground state contribution to the pump–probe signal agree with the classical predictions and show that $\delta g_q$ can be narrower than the zero point level probability distribution. These computations are compared to the femtosecond transient dichroism signals observed for I$_2$ in hexane reported by Scherer, Jonas, and Fleming (J. Chem. Phys. 1993, 99, 153–168) and found to agree within experimental error. The quantum calculations also show the thermal simplification of the pump–probe signal toward the classical limit as temperature is increased. We show quantitatively that for an electronically resonant pump-pulse, $\delta g_q$ tends toward a negative operator (a “pure ground state hole”) with increasing temperature, implying that certain types of pump–probe signals (e.g. photon-detected transient absorption) have signed ground state signals which do not oscillate through zero.

I. Introduction

Pump–probe spectroscopy with femtosecond lasers typically involves optical pulses which are shorter than the period of low-frequency (hundreds of cm$^{-1}$) molecular vibrations. It is well-known that such short pulses, which we will call “vibrationally abrupt”, create vibrational wavepackets on both the ground and excited electronic states.$^1$–$^5$ Some femtosecond experiments employing ionization or fluorescence detection$^6$–$^8$ are sensitive only to the excited state wavepacket, but experiments which detect changes in the probe beam (e.g. transient absorption,$^4$ transient dichroism,$^4$ transient off transient gratings$^9$) are typically a sum of quantum beat like signals from both ground and excited state wavepackets. Separating the signal into ground and excited state contributions is often a major difficulty in interpreting pump–probe experiments. A number of questions arise: Does the wavepacket increase or decrease the amount of light reaching the detector? Can one distinguish a half-period delay in wavepacket appearance from a wavepacket which has the opposite effect (e.g. increase rather than decrease) on the amount of light reaching the detector? Are the beat frequencies fundamental vibrational frequencies or higher harmonics? It is easy to visualize and understand how absorption creates an excited state wavepacket, but there does not seem to be agreement on what, exactly, the ground state wavepacket is: the ground state wavepacket must include the movement caused by resonant stimulated Raman scattering, but does it include the absorptive bleach or the ground state population remaining after the pump? It is perhaps surprising that a classical picture which apparently neglects Raman scattering entirely is helpful for understanding how both ground and excited state wavepackets are created by and interact with electronically resonant, vibrationally abrupt, optical pulses. This classical model also leads to a natural and useful definition of the ground state wavepacket. (We clarify the apparent paradox of how absorption alone can explain a Raman scattering effect in the Discussion.) The classical model explains how the time intervals between vibrational beats in the pump–probe signal depend on the pump and probe wavelengths and in particular how the dominant beat frequency is sometimes double the vibrational frequency. The classical model also predicts an optimum pulse duration for creating (and probing) the sharpest wavepackets. As illustrated here with full quantum mechanical calculations of iodine pump–probe signals, these predictions of the classical theory are essentially accurate at high temperature $kT >> \hbar \omega$ and make useful predictions even at $T = 0$.

We emphasize what the pump-induced change in the density operator, $\delta g_q$, looks like and how a particular pump–probe detection scheme samples $\delta g_q$ because it can be shown that all pump–probe signals depend only on $\delta g_q$. The pump-induced change in the density operator can be split (neglecting electronic coherences) into the change in the excited state vibrational density matrix $\delta g_q$ and the change in the ground state vibrational density matrix $\delta g_q$. A plot of the time evolution of $\langle R | \delta g_{q,R} | R \rangle$ created by femtosecond excitation of the visible electronic absorption band of iodine at room temperature is shown in Figure 1. $\delta g_q$ is essentially negative; it looks like a hole that develops during the pump pulse and then periodically oscillates from side to side. $\delta g_q$ (not shown) is positive and looks like an oscillating wavepacket. If $\delta g_q$ is what we call a pure hole,$^{10}$ this can help in sorting out the ground and excited state contributions to experimental pump–probe data because a pure ground state hole can only decrease the ground state absorption.

* Correspondence address: Department of Chemistry, The University of Chicago, 5735 S. Ellis Ave., Chicago, IL 60637. (312) 702–7068.
Femtosecond Wavepacket Spectroscopy

Figure 1. Plot showing the pump-induced change in the coordinate probability density \( (R|\delta \rho_{g}|R) \) as a function of time. \( R \) is the change in the ground state vibrational density matrix caused by a pump pulse resonant with the \( I_1 \) B-X band. The \( R \) axis ranges from 2.3 to 3.1 Å, and the time axis ranges from 0 to 395 fs. The near edge of the mesh by the 580 nm, 30 fs duration pump pulse and then oscillates from large \( R \) to small \( R \) and back with a period of 157 fs. \( (R|\delta \rho_{g}|(t|R) \) is mainly negative although small positive regions can be seen on close inspection.

We will examine more closely the question of whether \( \delta \rho_{g} \) is purely a “hole” or also contains some “particle” character (it turns out to depend on temperature) and concentrate on ground state wavepackets because the case of a ground state hole is subtle and illustrates several important limiting behaviors. When the ground state hole becomes a pure hole, it is simply the opposite of an excited state wavepacket. Therefore, our conclusions about (i) how the quasi-classical motion and spreading of the hole determine the form of the pump-probe signal, (ii) the role of temperature in simplifying the pump-probe signal, and (iii) the effect of pulse duration apply to the excited state wavepacket as well as the ground state hole. Many workers have used classical treatments of excited state wave-packet signals to help interpret experimental data. However, the ground state signals at low temperature have a peculiar feature: they can both increase and decrease (at different times) the absorption of the probe beam by the sample.

A number of papers on femtosecond wavepackets are related to our work. Walsmsley et al. observed femtosecond oscillations in transient transmission which they attributed to vibrational wavepackets whose origin could not be determined from the femtosecond experiments alone. They modeled the femtosecond quantum beats with two vibrational levels for each Raman active normal coordinate in each electronic state. We are concerned with vibrationally abrupt pulses which may excite coherent superpositions involving several vibrational levels. Dunn et al. used fluorescence upconversion to observe oscillations in excited state wavepacket spontaneous emission from gas-phase Na\( _2 \) and discussed the wavepacket dynamics in some detail. Nelson and co-workers have used off-resonant pulses to create ground state vibrational wavepackets through impulsive stimulated Raman scattering. Banin and Ruhman report vibrational beats attributed to coherent vibration of the \( I_1^- \) photoproduction and the ground state of \( I_1^- \) following femtosecond photodissociation of triiodide anions. In a preliminary report of the work described in this paper has already appeared, as has some closely related work by Smith, Cina, and Ungar exploring the ground state effects of electronically resonant single pulses and phase-locked pulse pairs.

II. Pump–Probe Experiments

In a time-resolved pump–probe experiment, the pump pulse modifies the sample, and one detects how this pump-induced change in the sample modifies the interaction between a sample and the probe. For example, in a transient absorption experiment, the pump–probe signal is the transient change in pump absorption caused by the pump, which can be detected by chopping the pump beam and feeding the output of a photomultiplier detecting the probe to a lock-in amplifier referenced to the chopping frequency. In transient dichroism, one detects the transmission of the probe through a pair of crossed polarizers surrounding the sample. This transmission would be zero except that pump photoselection of molecular alignment allows the photoslected molecules to rotate the probe polarization; therefore, transient dichroism is also a change caused by the pump. The same argument applies to probe diffraction off a pump-induced transient grating, since the grating does not exist without the pump. Time-resolved pump–probe spectroscopies detect only a change caused by the pump. In section IV, we shall show that this allows any pump–probe signal to be calculated from the change in the density matrix caused by the pump, \( \delta \rho_{g} \).

If optical coherence can be neglected (either because it is averaged out by the experimental apparatus or because of optical dephasing), then we can consider the changes in the density submatrices for the ground and excited states separately. Each vibrational density matrix has all the properties of a density matrix except normalization (the sum of the two vibrational density matrices is normalized). This use of separate changes in the vibrational density matrices has the advantage that we can break the transient absorption signal (or any other pump–probe signal) down into three decoupled parts: (1) the change in the absorption by the ground state, which is governed by the change in the vibrational density matrix of the ground electronic state, \( \delta \rho_{g} \); (2) the change in the stimulated emission from the excited state, governed by the change in the vibrational density matrix for the excited electronic state, \( \delta \rho_{e} \); and (3) the change in absorption by the excited state (which populates doubly excited electronic states), also determined by \( \delta \rho_{e} \).
It is important to be clear what we mean by a change in absorption or stimulated emission, since the term absorption is often used to refer to net positive absorption (absorption minus stimulated emission) and the term stimulated emission is often used to refer to net positive stimulated emission (stimulated emission minus absorption).20 We refer exclusively to the individual processes given by the Einstein coefficients \( B_{\text{e}} \) for stimulated emission and \( B_{\text{a}} \) for absorption.27 Stimulated emission then depends only on the populations of the upper state, and absorption depends only on the population of the lower state (only the net rates depend on the population difference). The total signal can be expressed as the change in net absorption, but the advantage of using separate stimulated emission and absorption terms is that they decouple the ground and excited states: the stimulated emission term in the pump–probe signal depends only on \( \delta Q_x \); the large equilibrium population of the ground state doesn’t affect this part of the signal. Similarly, the change in the ground state absorption is determined solely by \( \delta Q_a \); the excited state wavepacket and its motion are irrelevant. Our discussion of this point has been deliberately careful because we believe a certain amount of confusion exists in the literature. It should be emphasized that the decoupling of absorption and stimulated emission discussed above is not appropriate if electronic coherence plays a role in the signal (e.g. photon echoes).

This division of the signal is especially useful if the separate contributions to the signal are signed (even though the total signal may not be). Since the excited state population is zero at thermal equilibrium, the change in stimulated emission from the excited state is necessarily positive and always acts to increase the number of photons in a probe beam passing through the sample. Similarly, absorption of the probe by the excited state can only decrease the number of probe photons. It is helpful to know that a signal is a sum of a positive signal and a negative signal due to distinct physical processes, since this places constraints on the interpretation and grouping of fit parameters. While many pump–probe detection schemes yield signed excited state signals, some do not.28 We give a criterion for signed excited state pump–probe signals later and emphasize that this issue requires a careful analysis of the pump–probe detection technique. For now we mention that transient absorption experiments in which the entire probe frequency spectrum is detected by a photomultiplier or photodiode with a flat spectra response yield signed excited state signals.

The sign of the ground state signal is more difficult to determine a priori because the equilibrium ground state population is not zero. We might expect the change in absorption by the ground state to be a decrease because the total ground state population has been reduced by the pump, but a coherent superposition of states created by stimulated Raman scattering might absorb wavelengths that the original state could not, thus increasing the ground state absorption. Such increases in absorption by the ground state might not be possible if all levels of the coherent superposition were initially thermally populated and also had population removed by the pump. The classical picture discussed in the next section suggests this conjecture of signed ground state signals is correct at high temperature. Clearly, some ground state signals are not signed at \( T = 0 \) if stimulated Raman scattering occurs, and the temperature dependence of the ground state signal requires careful scrutiny to determine if the ground state signal is signed. Regardless of whether the ground state signal is signed or not, absorption and stimulated emission are independent: a ground state wavepacket does not affect the stimulated emission from an excited state wavepacket (and vice versa for absorption).

![Figure 2](image-url)

**Figure 2.** Illustration of the classical Franck principle for the visible B–X electronic absorption spectrum of \( I_2 \). The solid curves are the gas-phase RKR electronic potential energy curves for the iodine B and X states as a function of the internuclear distance \( R \). The dashed line above the X state marks the total energy, \( E \), of a classical trajectory. The dashed line above the B state curve, obtained by adding the kinetic energy at each point on the ground state trajectory to the B state curve, marks the total energy which classically conserves both nuclear position and momentum during B–X electronic absorption. At each \( R \), the difference between the two dashed curves, which is equal to the electronic energy gap \( (V_B(R) - V_X(R)) \) between the two potentials, dictates the wavelength of light which is absorbed. The trajectory shown absorbs 580 nm light at its outer turning point \( (R = 2.74 \text{ Å}) \), 521 nm light as it crosses the equilibrium bond distance \( (R = 2.67 \text{ Å}) \), and 480 nm light at the inner turning point \( (R = 2.60 \text{ Å}) \). Note that absorption of wavelengths shorter than 480 nm and longer than 580 nm is not possible for a molecule on the dashed trajectory.

### III. Classical Picture

Heller and co-workers29,30 have emphasized the conceptual advantages of classical and semiclassical pictures of spectroscopy. In the high temperature limit, classical treatments of ensemble nuclear motion can be used to quantitatively calculate molecular spectra.31,32 The quantum density operator, \( \varrho \), becomes the phase space density \( \varrho(q,p) \) in the classical limit, and the classical limit of the Franck–Condon principle33 gives a simple picture of how absorption and emission of light depend on position and momentum which can be used to gain considerable insight into pump–probe spectroscopy. The phase space density, \( \varrho(q,p) \), gives the probability distribution for finding a particle at position \( q \) and momentum \( p \). The classical Franck principle34 (the classical limit of the Franck–Condon principle35) states that nuclear position and momentum cannot change during the sudden optical transition between electronic states. This implies that the nuclear kinetic energy is conserved so that the photon energy must match the electronic energy gap at the instantaneous nuclear position.

\[
hv = [V_B(q) - V_X(q)]
\]

(1)

The classical Franck principle says that the instantaneous internuclear geometry dictates what wavelengths of light can be absorbed, as illustrated in Figure 2. It is important to note that eq 1 does not depend on the momentum: the time average which biases CW absorption spectra toward extrema of the difference potential \( [V_B(q) - V_X(q)] \) for a particular trajectory (such as classical turning points) becomes irrelevant for vibrationally abrupt pulses. A vibrationally abrupt pump pulse will electronically excite molecules which happen to be at coord-
Femtosecond Wavepacket Spectroscopy

Figure 3. Pictorial representation of classical wavepacket creation (left) and wavepacket motion (top to bottom at right) in phase space. The equilibrium phase space density \( \rho_{\text{eq}}(q,p) \) of the ground state is shown at the upper right. A pump pulse window function \( w(q) \) showing the range of coordinates within which molecules can be instantaneously excited by the pump spectrum is shown below \( \rho_{\text{eq}}(q,p) \). The pump-induced change in phase space density \( \delta \rho(q,p) \) is given at the lower left (assuming no motion takes place during the pump pulse). In this approximation, the change in the ground state phase space density \( \delta \rho_{\text{eq}}(q,p) = -\delta \rho(q,p) \) is negative and equal and opposite to \( \delta \rho_{\text{eq}}(q,p) = +\delta \rho(q,p) \), the change in the excited state phase space density. At the right, we show (from top to bottom) the motion of \( \delta \rho(q,p) \) as a function of time from \( t = 0 \) to half the vibrational period. In dimensionless normal coordinates, harmonic oscillator motion in phase space is just rigid rotation about the origin. The wavepacket’s projection onto the \( q \) axis in coordinate space moves from side to side and alternately expands and contracts twice per vibrational period. The ground state pump-probe signal may be approximately calculated from the overlap between \( \delta \rho_{\text{eq}}(q,p) \) and a probe window function centered at the coordinates where the probe frequency satisfies eq 1. The excited state pump-probe signal may be calculated in the same manner except that the change in excited state phase space density, \( \delta \rho_{\text{ex}}(q,p) \), rotates about the excited state vibrational equilibrium.

nates where the electronic energy gap equals the photon energy. Because short pulses have a frequency spread, they can excite (and are sensitive to) molecules within a range of instantaneous nuclear geometries. The width of this range is approximately given by the pulse frequency spread divided by the slope of the difference potential at the point where the pulse center frequency obeys eq 1. For a “vibrationally abrupt” pulse, molecules simply do not have time to move into or out of the range of internuclear coordinates sampled by the pulse. We are thus led to expect that a vibrationally abrupt pump pulse will create a localized wavepacket on the excited electronic state and a complementary localized bleach or hole in the ground electronic state: see Figures 2 and 3. Since they are not at equilibrium, both the excited state wavepacket and the ground state hole move and spread on their respective potentials. We find it easiest to visualize movement (and especially spreading) of the wavepacket (or hole) in classical phase space. At high temperature \( (kT >> \hbar \omega) \), one expects the classical picture of ground state holes and excited state wavepackets to predict the optical frequency which creates or probes wavepackets (or holes) at a given location with an accuracy of about a vibrational quantum.

If we know the pulse spectrum and the potential surfaces, we can easily predict the range (or ranges) of internuclear geometries that a pulse probes from eq 1 as shown in Figure 2. For the moment, we neglect changes in position and momentum during the pulse; then the pump pulse moves molecules which instantaneously obey eq 1 from the ground state to the excited electronic state, creating a localized hole in the ground state phase space density, \( \delta \rho_{\text{eq}}(q,p) \), which is equal and opposite to the positive phase space density created on the excited electronic state, \( \delta \rho_{\text{ex}}(q,p) \). This wavepacket creation in classical phase space is shown schematically in Figure 3. The pump-probe signals for multidimensional excited state wavepacket motion on anharmonic potentials have been discussed by Marcus using action-angle variables. For a harmonic oscillator, the Hamiltonian makes the phase space density move rigidly in a circle (we use dimensionless normal coordinates) about the point \( (q = R_{\text{eq}}, p = 0) \), as shown in Figure 3. This rigid rotation in phase space causes periodic oscillation and spreading of the wavepacket (or hole) in coordinate space. The classical pump-probe signal is proportional to the overlap between \( \delta \rho_{\text{eq}} \) and the range of coordinates sampled by the probe pulse and will have maxima whenever the wavepacket makes its closest approach to the probed region. The width of these peaks in the pump-probe signal is determined by both the width of the wavepacket and the range of coordinates sampled by the probe: steeper difference potentials yield sharper pump-probe signals from a smaller range of coordinates. If we consider a pump pulse at the side of the vibrational well, the first approach to the probed region will occur after a delay \( d \) (which must be less than half a vibrational period); there will be maxima in the classical pump-probe signal at times

\[
t = d, (T - d), (T + d), (2T - d), (2T + d) \ldots
\]

where \( T \) is the vibrational period. For example, if the delay is zero (pump and probe identical), we have pump-probe maxima at \( t = nT \). A more interesting case occurs for a delay of a quarter period, so that we have maxima at \( (2n + 1)T/4 \) and the dominant beat frequency is double the vibrational frequency. All delays other than \( T/4 \) can yield classical signals with strong Fourier components at both the first and second harmonics of the vibrational frequency. Because the classical pump-probe signals can have sharp, unequally spaced maxima, it is clear that the Fourier transform of even a simple pump-probe signal can contain many harmonics of the vibrational frequency.

IV. Quantum Mechanical Picture

The density operator for an ensemble is defined by \( \rho = \sum \rho_{\psi} |\psi\rangle \langle \psi| \) where \( \rho_{\psi} \) is the probability of the state \( \psi \) with projection operator \( |\psi\rangle \langle \psi| \) in the ensemble. It is important to note that the states \( \psi \) need not be eigenstates or even orthogonal to each other, but the probabilities must sum to 1 (\( \sum \rho_{\psi} = 1 \)). In terms of the density operator, the expectation value \( \langle M \rangle \) of an operator \( M \) is given by \( \langle M \rangle = \text{tr}(\rho M) \), where \( \text{tr} \) denotes the trace (i.e. sum of diagonal matrix elements).

In general, the pump-probe signal, \( S_{\text{pp}} \), is proportional to the difference between the probe signals obtained with and without the pump:

\[
S_{\text{pp}} = S_{\text{pump} + \text{probe}} - S_{\text{probe only}}
\]

Making use of the density matrix equations \( S_{\text{probe only}} = \text{tr}(\rho^{(0)} M) \) and \( S_{\text{pump} + \text{probe}} = \text{tr}(\rho M) \), where \( \rho \) is the density operator after the pump pulse and \( \rho^{(0)} \) is the density operator in the absence of the pump (e.g. the equilibrium density operator \( \rho_{\text{eq}} = (1/...) \)
we let the number of probe photons absorbed without the pump. If is the vibrational eigenstate of the molecule, we can use the propagator of the density matrix to calculate the pump-probe signal. The calculation proceeds from eq 3 as

$$S_{pp} = \text{tr}(\delta \rho M)$$  (4)

with

$$\delta \rho = (\rho - \rho^{(0)})$$  (5)

Because the relationship between any observable and the density operator is linear, all pump-probe signals can be obtained from the pump-induced changes in the density operator, \(\delta \rho\), no matter what detection scheme is employed.

The classical theory leads us to expect that for electronically resonant pulses \(\delta \rho\) should become a particle-like excited state wavepacket plus a hole-like ground state wavepacket. The vibrational density matrices \(\rho_e\) and \(\rho_g\) have all the properties of a density matrix except normalization, but the pump-induced changes in the vibrational density matrices, \(\delta \rho_e\) and \(\delta \rho_g\), have somewhat different properties. The matrix \(\delta \rho_e = \rho_e - \rho_e^{(0)}\) for the excited state is a vibrational density matrix since \(\rho_e^{(0)} = 0\). However, \(\delta \rho_g\) is not a vibrational density matrix because \(\rho_g^{(0)} \neq 0\). As discussed in section II, if \(\delta \rho_g\) were a pure hole, this would guarantee that the ground state wavepacket would always increase the sample transmittance in the same way that stimulated emission from the excited state wavepacket always increases the sample transmittance and absorption by the excited state wavepacket always decreases the sample transmittance. At zero temperature, the ground state wavepacket is not simply a hole because the coherent superposition state created by stimulated Raman scattering may absorb light at wavelengths which the zero-point level cannot, thus decreasing the transmittance. However, the room temperature image of \(\langle R | \delta \rho_g | R \rangle\) in Figure 1 certainly looks close to the pure hole classical mechanics leads us to expect. We have used numerical quantum calculations of the 1s pump-probe signal to explore the validity of the classical picture and the temperature dependence of the pump-probe signal.

Because we are interested in a thermal averaging effect, we find it computationally expedient to calculate the pump-probe signal from each vibrational eigenstate and then perform a Boltzmann-weighted sum to get the observed signal. This strategy avoids repeating the integration over the optical fields that would be necessary at each temperature in a direct density matrix calculation. The disadvantage of using the density operator only as a conceptual and analytic tool is that interactions with the environment (which we ignore) are not taken into account during the optical pulse (although damping could be easily included between pulses by forming the density matrix after the first pulse, propagating the density matrix between pulses (e.g. Bloch equations, Redfield theory), and then decomposing the density matrix into coherent states/eigenstates before the second pulse). No treatment of relaxation phenomena is included in the calculation of the ground state signals shown here; this is reasonable in light of the experimental assignment of the slow damping of the 1s ground state transient dichroism signal as mainly rotational realignment rather than vibrational population relaxation or pure vibrational dephasing.

The specific pump-probe signal we calculate detects probe photon number, so that the pump-probe signal is proportional to the number of probe photons absorbed with the pump minus the number of probe photons absorbed without the pump. If we let \(\Psi_g^{(0)}(t)\) be the ground state wavepacket created from vibrational eigenstate \(\phi\) by the pump, the ground state signal is

$$S_{pp} = -\sum_i p_i (\langle e_i | U_{probe} \Psi_g^{(0)}(t) | e_i \rangle)^2 - \langle e_i | U_{probe} \phi | e_i \rangle^2$$  (6)

where the sum is over vibrational levels of the ground state (with population \(p_i\) and excited state levels \(e_i\). \(U_{probe}\) is the probe pulse propagator. Note that we have taken the proportionality constant to be \(-1\) (to match the experimental transient dichroism signals and equated photon number destroyed with population created on the excited state. Equation 6 defines a pump-induced increase in the number of probe photons reaching the detector as a positive signal.

The sums in parentheses can be rearranged to put equation 6 into a density matrix format. For the second term on the right-hand side of eq 6 we have

$$\sum_i \langle e_i | U_{probe} \Psi_g^{(0)} | e_i \rangle^2 \langle e_i | U_{probe} \phi | e_i \rangle - \sum_i \langle e_i | U_{probe} \Psi_g^{(0)} | e_i \rangle \langle e_i | U_{probe} \phi | e_i \rangle$$

by the definition of the density matrix. We can expand the sum over levels of the excited electronic state to a sum over all states by using the projection operator \(P_e\), which has the property that \(P_e | j \rangle = \delta_{|j|} | e \rangle\).

$$\sum_i \langle e_i | U_{probe} \Psi_g^{(0)} U_{probe} | e_i \rangle = \sum_i \langle e_i | U_{probe} \Psi_g^{(0)} U_{probe} | e_i \rangle = \sum_i \langle e_i | U_{probe} \Psi_g^{(0)} U_{probe} | e_i \rangle$$

Finally, we can put eq 8 into the standard form by using the equality \(\text{tr}(AB) = \text{tr}(BA)\) characteristic of the trace.

$$= \text{tr}(\rho^{(0)} U_{probe} P_e U_{probe})$$  (9)

(We have also used the relationship \(P_e^2 = P_e\) for projection operators.) The first term on the right-hand side can be rewritten similarly, so that the ground state pump-probe signal is thus

$$S_{pp} = -\sum_i p_i (\langle e_i | U_{probe} \Psi_g^{(0)}(t) | e_i \rangle)^2 - \langle e_i | U_{probe} \phi | e_i \rangle^2$$  (6)

Although eq 10 has the usual density matrix form (i.e. that of eq 4), the more symmetrical form of eq 8 will be useful later in discussing the sign of the signal and its relationship to the concept of a ground state hole. In the short pulse limit, \(P_e U_{probe}\) becomes (interaction picture) \(P_e U_{probe}\) for projection operators. The first term on the right-hand side can be rewritten similarly, so that the ground state pump-probe signal is thus

$$S_{pp} = -\sum_i p_i (\langle e_i | U_{probe} \Psi_g^{(0)}(t) | e_i \rangle)^2 - \langle e_i | U_{probe} \phi | e_i \rangle^2$$  (6)

**IVA. Methodology.** We start by calculating the effect of the pump pulse on each ground state eigenstate, \(\phi\), and form \(\Psi_e^{(0)}(t)\) and \(\Psi_g^{(0)}(t)\) during and after the pump pulse. From these \(\rho_e\), \(\rho_g\), and \(\delta \rho_g\), can be formed; for example \(\langle R | \delta \rho_g | R \rangle\) shown in Figure 1 is constructed from \(\Psi_g^{(0)}(t)\) as follows:

$$\langle R | \delta \rho_g | R \rangle = \langle R | \rho_g | R \rangle - \langle R | \rho_g^{(0)} | R \rangle$$

$$= \sum_i p_i \langle R | P_e \Psi_e^{(0)}(t) \Psi_g^{(0)}(t) | R \rangle - \sum_i p_i \langle R | \phi | R \rangle \langle R | \phi \rangle$$  (11)

Calculation of the pump-probe signal proceeds from eq 6. As the probe field is time dependent, eq 6 contains a time integration over the probe pulse which is hidden in the probe propagator. To calculate the pump + probe signal, we can propagate each \(\Psi_i^{(0)}(t)\) through the probe interaction and identify the population transferred at the end of the probe pulse. To calculate the ground state signal, for example, we zero out the
excited state amplitude after the pump pulse is over, propagate through the probe pulse, and store the population on the excited state after the probe pulse is complete as the signal for that pulse delay. This is done for each interpulse delay and for each initial eigenstate \( \phi_i \). The probe only transition probability is calculated once only for each state \( \phi_i \) in the same manner as the pump + probe signal. The overall signal is formed from eq 6. By blanking out the excited state amplitude prior to the probe interaction, we eliminate effects of interference between the ground and excited state wavepackets created by the pump pulse during the probe pulse. This is in accord with experiments that typically average over the pump/probe pulse phase relationship and thus lose this interference contribution to the signal; this would not be the case if the relative phase of the pump and probe pulses were locked.\(^{25} \) The signal due to the probe pulse could be approximated by use of a window function which is evaluated on a grid by the fast Fourier transform method.\(^{51} \) Convergence for the energy levels of a Morse oscillator when the initial eigenstates, \( \Psi_\ell \left( \tau \right) \) and \( \Psi_p \left( \tau \right) \), were computed using the Numerov-Cooley method\(^{51} \) with the simplification introduced by Ross.\(^{52} \) The conversion of eq 12 to an iterative scheme follows Kosloff;\(^{42,43} \) the time propagator is approximated by second-order differencing, and the nuclear kinetic energy operator \( T \) is evaluated on a grid by the fast Fourier transform method.\(^{44} \) The ground–excited state coupling by the pump and probe pulses is given, for the pump pulse case, by \( \mu E_{\text{pu}} \), where \( \mu \) is assumed to be independent of the internuclear distance (Condon approximation),\(^{45} \) and \( E_{\text{pu}} \left( t \right) \) is

\[
E_{\text{pu}} \left( t \right) = E_0 \cos \left[ \omega_{\text{pu}} \left( t - t_{\text{pu}} \right) \right] e^{-\left( t-t_0\right)/2\tau_{\text{pu}}^2}
\]

The parameters used for the pulses are \( \mu E_0 = 0.0001 \text{ au} \) and \( \tau = 18 \text{ fs} \) (the pulse intensity fwhm = 2\( \sqrt{\ln(2)} \) \( \tau \) is 30 fs) for both pump and probe. We have verified that these fields are “weak” by reducing \( \mu E_0 \) by an order of magnitude and checking that the pump–probe signals are identical. \( \omega_{\text{pu}} \) and \( \omega_{\text{pe}} \) are chosen to match the wavelengths used in the experiments.\(^8 \)

The functions \( V_g \left( R \right) \) and \( V_e \left( R \right) \) are the gas-phase potentials for the \( X \) and \( B \) states of \( \text{I}_2 \). The shifts to the potentials due to the solvent (hexane) are assumed equal, and the potentials are not expected to be significantly deformed (at least around the ground state equilibrium internuclear distances) from the gas-phase curves. The functions are 13th-order Lagrange interpolations to the RKR potentials,\(^{47} \) which we found to yield optimal convergence for the energy levels of a Morse oscillator when treated as an RKR test data set. The bound portion of the \( B \) state potential is from Barrow and Yee;\(^{48} \) the repulsive portion of the \( B \) state potential was taken from the paper by Brand et al.\(^{49} \) and was smoothly incorporated to the RKR points by a switching function. The \( X \) state potential is from LeRoy.\(^{50} \) The initial eigenstates, \( \Psi_e \left( 0 \right) = \phi_i \), were computed using the Numerov–Cooley method\(^{51} \) with the simplification introduced by Ross.\(^{52} \) Convergence and the accuracy of the interpolated RKR potentials were tested for by comparison of the energy levels and rotational constants to the experimental results.\(^{53,54} \) Only the initial states \( v = 0, 1, 2 \) and 3 have significant Boltzmann weight at room temperature. Higher initial vibrational levels are calculated for the results discussed in section VI.

The method used to calculate the \( \text{I}_2 \) pump–probe signals is entirely quantum mechanical; the evaluation of the Hamiltonian and the time propagation is general for any potential or time-dependent interaction. This allows us to study the effect of changing the potential or of changing the femtosecond pulse durations and pulse shapes. Efforts to reduce the computation time beyond normal optimization of the time step and grid intervals were not required; a number of improvements or approximations to the time propagator would have no doubt given better results with considerably faster performance.

### V. Results

In this section we present calculations of the pump–probe signals from ground state wavepackets in molecular iodine, demonstrating the variation of the transients with pump and probe wavelength, temperature, and pulse duration. As we shall see, the high temperature results bear out the major predictions of the classical model discussed in section III, but the limitations of the classical model become apparent at low temperature. The simulations are compared with fixed pump, tunable probe experimental transient dichroism signals from room temperature \( \text{I}_2 \) in hexane;\(^8 \) the overall agreement is very good.\(^{52} \) In the 580 nm pump/580 nm probe signal, the classical model predicts that a ground state hole will be created at the outer wall of the \( X \) state by the pump and probed once per vibrational period each time it returns to the outer wall (i.e. at \( t = 0, T_{\text{vib}}, 2T_{\text{vib}}, 3T_{\text{vib}}, \ldots \)). The calculated signal shown in Figure 4 agrees with this classical expectation at 300 K, but the signal at lower temperatures oscillates through zero, indicating that the ground state wavepacket sometimes decreases the amount of probe light reaching the detector. At \( T = 0 \), the ground state signal (from \( v = 0 \) oscillates about zero, proving that \( \delta q_x \) is not purely a hole, since we show later that a pure hole can only increase the probe transmission. The temperature dependence is enlighten-
positive side lobes when near the turning points at 149 fs (86
entirely signed. The pulse is centered at 63.5 fs.
the range in
the calculated signal contains significant amplitude at both the
fundamental and second harmonic of the ground state frequency.

As
vibrational levels of the ground state contribute substantially
through zero. The sharp maxima
which occur only once per vibrational period, so that the signal
maxima are sharper than a single sine wave. The sharp maxima
in Figure 4 indicate that the ground state wavepacket is narrow.

We have plotted \(|R|\langle\delta Q_2|R\rangle\), the coordinate space image of
\(\delta Q_2\) at 300 K for a series of times, in Figure 5 (this is the same
object plotted in Figure 1). The creation and time evolution of
\(|R|\langle\delta Q_2|R\rangle\) clearly fit in well with the classical expectations
discussed above. As can be clearly seen, \(|R|\langle\delta Q_2|R\rangle\) has small
positive side lobes when near the turning points at 149 fs (86
fs after the pump maximum) and 223 fs (160 fs after the pump
maximum). At other times, \(|R|\langle\delta Q_2|R\rangle\) looks negative. The 580/
580 pump–probe signal is positive at 300 K despite these small
side lobes. The narrow pump–probe maxima evidently reflect
the narrow width of \(|R|\langle\delta Q_2|R\rangle\) at the outer turning point. In
fact, the full width at half-maximum for \(|R|\langle\delta Q_2|R\rangle\) at the turning
points is 0.06 Å at the left and 0.07 Å at the right, which are
both smaller than the 0.085 Å fwhm of the probability distribution
(i.e., \(\psi^2\)) for the zero-point level. The preparation of such
"squeezed" wavepackets on the excited state has been theoretically
discussed by Vinogradov, Janszky, and co-workers.55

In a preliminary report,22 experimental transient dichroism
signals were compared to calculated signals by simply overlaying
the two transients. The computational results matched experiment well, although the excited state signal present in
the experimental data complicates the comparison for small
pump–probe delays. In Table 1 we compare experiment and
simulation more precisely: the experimental linear prediction–
singular value decomposition (LP-SVD) amplitudes, frequencies,
and phases which had been assigned to the ground state8 are
listed side by side with a similar decomposition of the calculated
signals. (Since the frequencies in the calculated signal are
known and damping is absent, the calculated signal was simply
run through the singular value decomposition linear least squares
part of the LP-SVD algorithm to obtain the amplitudes and
phases.) From LP-SVD fits to a few experimental 580/580
transient dichroism data sets, Scherer, Jonas, and Fleming8
estimated an LP-SVD phase angle error bar of about 20° (or
18 fs delay for a 213 cm\(^{-1}\) vibrational frequency). There is
about 5 fs step-size error in determining the maximum "instantaneous electronic response" used as the experimental time zero.
The 580/580 data show good agreement between experiment
and calculation; the greatest discrepancy is for the amplitude
of the ground state fundamental vibrational frequency. It should
be noted that the LP-SVD analysis of the transient dichroism
data recovered both the dominant fundamental vibrational
frequency and the weaker second harmonic.
Femtosecond Wavepacket Spectroscopy

With a 526 nm probe, the classical picture predicts that the hole should be probed near the middle of the ground state well twice per vibrational period after an initial delay of about a quarter vibrational period (i.e., two maxima per vibrational period). The calculated signal is in excellent agreement with this expectation (Figure 6). The phase of the doubled frequency (−185°) reflects the classical delay of about a quarter vibrational period required for the hole to move from the outer wall, where it is created by the 580 nm pump pulse, to the center of the well, where it is probed by the 526 nm probe pulse. The doubled frequency is apparent at all temperatures, and in this case the signal happens to be positive at \( T = 0 \) K even though we have seen from Figure 4 that at \( T = 0 \) the \( \sigma_{0k} \) created by the 580 nm pump pulse is not purely a hole. In addition to the dominant component at the second harmonic of the ground state vibrational frequency, there is some amplitude at the first and third harmonics which serves to shift the signal maxima so that they occur in nearly symmetrical doublets: backward extrapolation of the Fourier components shows that the first maximum occurs slightly before \( T_{vis} / 4 \).

The doublets are also prominent in the experimental transient dichroism signal (see Figure 7 of ref 8). For the 580/526 data, overlaying experiment and calculation suggests that the time zero used in the LP-SVD fitting was about 64 fs before the true time zero (this has not been corrected for in Table 1). Because the 580/526 transient dichroism signal had three large spikes near the maximum pump–probe cross correlation, it seems possible that the “instantaneous electronic response” used to locate time zero was misidentified. If this hypothesis is correct, the agreement between experimental and calculated signals is good (see Figure 6 of ref 22).

The absolute value of the calculated ground state signal is weaker at this wavelength than at 580/580 (by a factor of 2) and that at 580/510 (by a factor of 1.5), in reasonable agreement with the estimated relative experimental intensities.

For the 580/510 experiment the classical picture predicts that the wavepacket generated at the outer wall will be probed between the center of the well and the inner turning point. The calculated signal in Figure 7 roughly matches this expectation, with broad asymmetric maxima occurring once per vibrational period after an initial delay of 64 fs, slightly less than 78 fs (half the vibrational period). The LP-SVD amplitude and phase extracted from the experiment roughly match the calculated signal, although the 45° phase mismatch for the 215 cm\(^{-1}\) component is larger than the estimated error. This phase mismatch could be a result of an error in time zero of about 19 fs, contamination by a second harmonic of the excited state vibrational frequency, or differences between the ideal transform limited pulses used in calculation and the actual pulses used in the experiment.

It seems to have been generally assumed that the vibrational frequencies obtained in femtosecond pump–probe studies are fundamental frequencies rather than higher harmonics. However, in the 580/526 data, the second harmonic was the dominant spectral component. Unless the vibrational displacements are small, the second harmonic is likely to dominate for pulses with center frequency near the absorption maximum. This will be especially true for the most convenient experimental configuration, the one-color pump–probe experiment with the center wavelength tuned to the absorption maximum. Classically, one expects to burn a narrow hole in the center of the potential well which will spread and contract twice per vibrational period. As an illustration of this, the calculated signal for 532 nm pump/532 nm probe is shown in Figure 8. The second harmonic of the vibrational frequency dominates the signal; the first harmonic might not even be detectable under the noise in an actual experiment. The 532 nm pumped signal is also larger in magnitude than the 580 nm pumped signal because 532 nm nearly coincides with the absorption maximum. Most of the 532/532 pump–probe signal comes from \( v = 0 \), which contributes a very large background relative to the vibrational modulation. We will discuss the reasons for this in the next section.

The temperature dependence of the 532/532 signal is quite interesting (see the Fourier transforms at 150 and 300 K in Figure 8). The ratio of first harmonic to second harmonic changes by a factor of 2 with temperature. This has a simple quantum mechanical explanation: since the pump and probe are tuned to the middle of the well, the levels with even vibrational quanta (which have amplitude in the middle of the well) are much more strongly coupled to the excited state by the optical field than the levels with odd quanta (which have a node in the middle of the well). Therefore, the strongest stimulated Raman scattering goes from even to even levels, \( \Delta v \)}
Figure 7. (left) Calculated temperature dependence and contributions (at 300 K) from each initial eigenstate for the I₂ 580/510 ground state pump–probe signal with 30 fs pulses; detail as in Figure 4. The maxima in the 580/510 signal occur between those in the 580/580 signal and are spaced one vibrational period apart. This suggests that the hole created at the outer wall by the 580 nm pump pulse is probed once per period near the inner wall after a delay of about a half vibrational period by the 510 nm probe pulse. The vertical axis has the same absolute scale as in Figure 4. (right) Fourier power spectrum of the 580/510 signal at 100 and 300 K.

Figure 8. (left) Calculated 532 nm pump/532 nm probe signal at 300 K (top panel, solid line), 100 K (top panel, dashed line), and Boltzmann-weighted pump–probe signal from each of the thermally populated eigenstates at 300 K (bottom panel). The signals from each eigenstate have been displaced so that zero coincides with the tick mark by the vibrational quantum number label. Note the huge offset for the v = 0 signal. Both pump and probe pulses are transform-limited Gaussian pulses centered at 532 nm with an intensity fwhm of 30 fs. The absorption maximum of the iodine B-X electronic absorption is near 532 nm, so 532 nm light is resonant near the center of the well. Note that the relative depth of the vibrational modulations compared to the static offset is lower for the center pumped signal than for the 580 nm pumped signals. The vertical axis has the same absolute scale as in Figure 4. (right) Fourier power spectrum of the calculated 532/532 pump–probe signal shown at 100 K (dashed line) and 300 K (solid line). The two power spectra are normalized so that the first harmonics have equal magnitude. The intensity of the second harmonic is about equal to the first harmonic at 100 K, but about twice as great as the first harmonic at 300 K. The second harmonic of the vibrational frequency dominates the 532/532 pump–probe signal because the hole created at the center of the well expands and contracts twice per vibrational period. The presence of the fundamental vibrational frequency in this signal indicates that the hole also moves from side to side. The breakdown by eigenstates (compare v = 0 and v = 1) shows why the ratio of the first and second vibrational harmonics depends strongly on temperature.

= 2 or more, explaining the dominant second harmonic. The v = 1 level contributes a smaller signal which is effectively nonresonant stimulated Raman scattering obeying a Δν = 1 selection rule.

We show the creation and subsequent evolution of ⟨R|dQ₃|R⟩ for a 30 fs pulse centered at 532 nm in Figure 9. In contrast to Figure 5, where ⟨R|dQ₃|R⟩ created by a 580 nm pulse began life at R ≈ 2.74 Å, here ⟨R|dQ₃|R⟩ starts out at R ≈ 2.68 Å and undergoes only a small side to side motion at the fundamental vibrational frequency which is about the same amplitude as the spreading and contraction. This wavepacket "breathing" at twice the vibrational frequency dominates the pump–probe signal. Because the hole never leaves the probe region, the pump–probe signal has a large background relative to the vibrational modulation. Note that ⟨R|dQ₃|R⟩ has a small positive side lobe 86 fs after the maximum pump intensity (at 149 fs in Figure 9).

We have seen in the above calculations that the low-temperature signals are complicated, but simplify toward the classical pump–probe signal (which may have Fourier components at both the first and the second harmonic) with increasing temperature. For the iodine ground state at room temperature, kₜ ≈ kT, and the classical picture is already very useful. Where the classical model predicts that we should probe the ground state wavepacket once per vibrational period, the intensity of the first harmonic grows relative to the second
VI. Temperature Dependence

In this section, we investigate the effect of temperature on the sign of the ground state signal and the hole-like character of $\delta Q_g$. Because the excited state vibrational density matrix $Q_e$ is positive, and $\delta Q_e = Q_e$, the pump-induced change in the excited state vibrational density matrix $\delta Q_e$ is positive. The positive property of $\delta Q_e$ guarantees that each pump–probe signal from the excited state is signed and does not pass through zero. For transient absorption, excited state absorption always increases the amount of light passing through the sample and excited state emission always increases the amount of light passing through the sample. (Absorption by the excited state and emission from the excited state are separate excited state signals, each is signed, but the sum of the two may not be.) Unlike $\delta Q_e$, $\delta Q_g$ is not a vibrational density matrix, but if $\delta Q_g$ is negative, $\delta Q_g$ is in some sense a negative density matrix.

As seen in Figure 4, the ground state pump–probe signal has an unusual temperature dependence in that although the ground state wavepacket usually increases the amount of light reaching the detector, the ground state wavepacket generated by a short pump pulse can sometimes decrease the probe transmission at low temperature. At high temperature, the classical theory leads us to expect that a pump pulse should create a hole in the ground state phase space distribution which can only increase the probe transmission, and the trend with temperature in Figures 4 and 7 seems to support this idea. A careful look at Figure 4 indicates that while all the calculated signals in Figures 4, 6, 7, and 8 are positive at 300 K, the expectation value of $\delta Q_e$ while mainly negative, does not follow on small positive values at some points in space and time. This does not fit very well with a (correct) expectation that for a hole $R|\delta Q_e| R$ must be negative at every point for all times. We want to guarantee that the measured value of any observable squared is negative. We show below that $\delta Q_g$ is a negative operator if and only if all the eigenvalues of $\delta Q_g$ are negative and that this guarantees that any observable squared is negative. This means that

$$\text{tr}(\delta Q_g | M |^2) \leq 0$$

for all observables $M$. Inequality 14 can be written in the form of eq 8:

$$\text{tr}(\delta Q_g | M |^2) = \text{tr}(\delta Q_g MM^*) = \text{tr}(M^* \delta Q_g M) \leq 0$$

Recall that this is the form of the ground state transient absorption signal if $M = P_{U_{probe}}$. If an observable $N$ obeys $\text{tr}(N) \geq 0$ for all positive density matrices $\rho$, then it follows from $\delta Q_g$ negative $[\delta Q_g$ positive] that $\text{tr}([\delta Q_g N] \geq 0)$. It should be emphasized that while many of the observables used to detect the pump–probe signal have this signed property (e.g. the total number of probe photons, the number of fluorescence photons, the number of ions), some do not (e.g. $\sin(\theta)$, where $\theta$ is the probe rotation angle in heterodyned transient dichroism, the number of probe photons in a specific frequency range), by making the substitution $|\psi\rangle = M|\phi\rangle$, inequality (15) is satisfied if we require

$$\langle \psi | \delta Q_g | \psi \rangle \leq 0$$

for every arbitrary state $|\psi\rangle$. Inequality 16 is simply a statement that $\delta Q_g$ is a negative operator. If $\delta Q_g$ is a negative operator, we are justified in calling $\delta Q_g$ a pure hole. Equation 8 shows that a negative $\delta Q_g$ will always increase the total number of photons passing through the sample, regardless of the probe parameters.

It is well-known that the elements of the density matrix must obey the inequality

$$Q_i Q_j \geq |Q_{ij}|^2$$

because $\rho$ is positive. The matrix elements of a negative operator also obey inequality 17, which leads directly to inequalities for the signal parameters in the optical Bloch limit (see section VII). However, the necessary inequality 17 is not sufficient to guarantee that $\rho$ is a signed matrix. A number of criteria are equivalent to positive definiteness ($\langle \psi | X | \psi \rangle > 0$ for all $|\psi\rangle$). On the basis of the discussion in ref 59, it is not hard to show that all the eigenvalues of the Hermitian operator

Figure 9. Plot of the change in the ground state coordinate probability density $R|\delta Q_e| R$ developed during and after the 532 nm 30 fs pulse; the pulse is centered at 63.5 fs. The hole is created near the ground state equilibrium internuclear distance; it primarily expands and contracts in time with some side to side motion. The extent of this side to side motion is considerably smaller than for the hole shown in Figure 5.
The simplest curve satisfying these constraints is bell shaped, with \( \text{tr}(\delta q_2)/\Sigma(\lambda) \) rising from zero as the wavelength approaches the absorption maximum and then falling back to zero. The larger ratio \( \text{tr}(\delta q_2)/\Sigma(\lambda) \) for 30 fs pulses centered at 532 nm as compared to 30 fs pulses centered at 580 nm is reflected in the smaller relative modulation depth of the 532/532 pump–probe signal.

For both \( \delta \) function pulses and CW excitation, we expect that \( \delta q_2 \) will be negative even at 0 K, since no stimulated Raman scattering occurs. This suggests that a graph of the minimum temperature at which \( \delta q_2 \) becomes a negative operator vs pulse duration should be some sort of bell-shaped curve. Smith, Ungar, and Cina have used an approximation to the second-order pulse propagator, which is valid for short pulses to investigate whether \( \delta q_2 \) obeys the necessary inequality \( \langle x|\delta q_2|x\rangle \geq \langle x'|\delta q_2|x'\rangle \) for a negative operator. They showed that when \( kt \gg \hbar \omega_{vib} \) and the range of pumped internuclear distances \( r \) is very much greater than the thermal de Broglie wavelength \( \Lambda = \left( \hbar^2/2\pi mkT \right)^{1/2} \), the necessary inequality is satisfied. These criteria seem very reasonable physically and suggest (but do not prove) that \( \delta q_2 \) is negative when \( kt \gg \hbar \omega_{vib} \) and \( r \gg \Lambda \). The relationships \( kt \gg \hbar \omega_{vib} \) and \( r \gg \Lambda \) help to describe the rising part of the bell curve when the pulse duration increases from zero. Our examination of the eigenvalues shows that, at 580 nm, a 60 fs pulse leads to a more negative \( \delta q_2 \) than a 30 fs pulse, and comparison of the calculated signals for 30 fs pulses with calculated pump–probe signals for 15 fs pulses suggests that \( \delta q_2 \) becomes more negative as the pulse becomes longer over the range 15 fs to CW. If \( \delta q_2 \) is very much greater than the frequency spread of the optical pulse, \( \hbar \Delta \nu \), stimulated Raman scattering can only create a coherent superposition of levels which have also been depopulated by absorption. We suggest that if \( kt \gg \hbar \Delta \nu \), \( \delta q_2 \) will be negative: this relationship seems to be a reasonable description of the tendency for longer pulses to yield a more negative \( \delta q_2 \) as the pulse approaches the CW limit. The relationship \( kt \gg \hbar \Delta \nu \) can be sharpened by taking into account Franck–Condon factors, which may only allow stimulated Raman scattering over a smaller range of energy than the frequency spread, \( \hbar \Delta \nu \), of the pulse. As will be seen in the next section, the optimum pulse duration for iodine will, ironically, require a higher temperature to guarantee a positive signal for easy data analysis.

**VII. Effect of Pulse Duration**

Other workers have noted that the wavepacket motion on the ground electronic state disappears for both infinitely short and infinitely long pulses. Vinogradov, Janszky, and co-workers have discussed the preparation of squeezed wavepackets (i.e., more narrow than \( \nu = 0 \) at some times) by femtosecond pulses in terms of quantum mechanical interference. The classical description allows one to understand the pulse duration dependence of the pump–probe signal in a transparent way and helps to quantify "too short" and "too long". Two competing effects yield an optimum pulse duration for creating narrow ground state wavepackets with transform-limited pulses: if the pulse is too short, it necessarily has a wide frequency spectrum and probes a wide range of coordinates; if a pulse is too long, molecules can move in and out of the probed range of coordinates during the pulse. Results of a calculation illustrating these effects for \( I_2 \) are shown in Figure 11. An infinitely short \( \delta \) function pulse bleaches all coordinates equally (neglecting variation of the electronic transition moment with electronic coordinates) and does not create a moving hole on the ground state. Roughly, a pulse is "too short" if the frequency spectrum covers more than half the absorption spectrum, since then it will bleach more than half of the thermally accessible coordinates. For iodine, a 6 fs pulse

---

**Figure 10.** Temperature dependence of the ratio \( \text{tr}(\delta q_2)/\Sigma(\lambda) \) used as a measure of the extent to which \( \delta q_2 \) is a negative operator (see text). This ratio is 0 for a completely unsigned matrix and 1 for a negative matrix. A negative \( \delta q_2 \) is a hole, and will give rise to a rigorously signed ground state pump–probe signal. Three different pump pulses are shown: (solid line) 30 fs pump pulse centered at 580 nm; (long-dashed line) 30 fs pump pulse centered at 532 nm; (short-dashed line) 60 fs pump pulse centered at 580 nm. As temperature increases, \( \delta q_2 \) becomes more negative in all three cases. From inspection of the eigenvalues, \( \delta q_2 \) is rigorously a negative operator at temperatures above 750 K for the 60 fs pulse.

\( \delta q_2 \) are negative or zero if and only if eq 16 is satisfied. We therefore focus on the eigenvalues of \( \delta q_2 \) as the most practical way to see if \( \delta q_2 \) is, in fact, a negative operator at high temperature.

We have chosen to show the ratio \( \text{tr}(\delta q_2)/\Sigma(\lambda) \) of the eigenvalues of \( \delta q_2 \) the trace is the sum of all the eigenvalues), as a measure of the extent to which \( \delta q_2 \) approximates a negative operator in Figure 10. Because the trace and the eigenvalues are invariant under unitary transformations, this measure is independent of time (in the absence of damping after the pulses are off) and independent of the basis set. In the weak field limit, \( \text{tr}(\delta q_2)/\Sigma(\lambda) \) is also independent of the pump pulse intensity. This ratio is bounded by 0 below (since it is easy to see that \( \text{tr}(\delta q_2) \) must be negative or zero in the eigenstate basis) and is equal to 1 for a negative matrix. The eigenvalues of \( \delta q_2 \) were obtained numerically from the matrix of \( \delta q_2 \) in the eigenstate basis at a single time \( t \). We examined the results of truncation at \( v = 4 \) and \( v = 6 \) and estimate that the eigenvalues are thermally converged up to about 1200 K. As can be seen in Figure 10, the ratio \( \text{tr}(\delta q_2)/\Sigma(\lambda) \) increases monotonically over the entire temperature range we have investigated, and \( \delta q_2 \) has become nearly negative for all three cases by 1200 K. For 60 fs pulses, inspection of the eigenvalues revealed that all the eigenvalues of \( \delta q_2 \) are negative by 750 K, proving that \( \delta q_2 \) becomes a negative operator above 750 K. For all three cases, but all three ratios indicate that \( \delta q_2 \) rapidly tends toward a negative operator starting at about 150 K, as the \( v = 1 \) state begins to be thermally populated. Although all four calculated pump–probe signals were taken at room temperature, the ratio \( \text{tr}(\delta q_2)/\Sigma(\lambda) \) of about 0.8 for 30 fs pulses indicates that \( \delta q_2 \) is only approximately a negative matrix at 300 K. For all three pulses, the ratio has reached 0.9 by 400 K.

The wavelength dependence of \( \text{tr}(\delta q_2)/\Sigma(\lambda) \) at a fixed temperature and pulse duration can be rationalized in the following way. For wavelengths both above and below resonance, \( \text{tr}(\delta q_2) = 0 \) since no population is removed from the ground electronic state. Since \( \text{tr}(\delta q_2) \) is negative in the resonance region, the simplest curve satisfying these constraints is bell shaped, with \( \text{tr}(\delta q_2)/\Sigma(\lambda) \) rising from zero as the
Figure 11. Calculated iodine ground state 580 nm pump/580 nm probe signals for several pulse durations at 300 K. Both pump and probe pulses are transform-limited Gaussian pulses with intensity fwhm $\Delta t$ shown at right. All signals have been plotted so that the maximum value of the pump–probe signal is 1. The optimum pulse duration results from a compromise between keeping pulses short to prevent molecules from moving in and out of the probed region during the pulse and keeping the frequency spectrum of the pulses narrow to avoid probing a wide range of coordinates with spectrally broad short pulses. These considerations predict that the optimum pulse duration should lie in the interval $(1/\Delta v_{\text{spectrum}}) < \Delta t < T_{\text{eq}}/2$, where $\Delta v_{\text{spectrum}}$ is the width of the absorption spectrum and $T_{\text{eq}}$ is the molecular vibrational period. A pulse duration of about 30 fs produces optimal vibrational wavepacket modulation of the signal, and the vibrational modulation of the signal is relatively insensitive to pulse duration over the range 15–60 fs. Note how the sharpness of the signal maxima changes, however, over this range of pulse durations.

centered at 580 nm covers roughly half the absorption spectrum. A pulse is too long if the pulse duration exceeds half a vibrational period, since this allows molecules to move into (or out of) the probed region from any part of the potential during the pulse. For the iodine 580/580 pump–probe transient, the ground state signal starts to wash out for pulses longer than $T_{\text{eq}}/2 = 78$ fs because a molecule can move all the way from the inner wall to the outer wall (or vice versa) in half a vibrational period. The vibrational modulation of the signal is relatively insensitive to pulse duration over the range 15–60 fs (i.e., near the middle of the interval $(1/\Delta v_{\text{spectrum}}) < \Delta t < T_{\text{eq}}/2$ containing the optimum pulse duration).

The classical model predicts that these criteria depend on pulse center wavelength and temperature and will be somewhat different for the excited state. For pulses tuned to the edge of the well, only half of the spectrum covers a populated range of coordinates and the other half does not widen the range of probed coordinates; in contrast, the entire spectrum of a pulse tuned to the center of the well contributes to the width of the probed range of coordinates. Pulses tuned to the absorption maximum require a more narrow frequency spectrum to avoid covering too broad a range of coordinates. However, molecules can move from any position on the potential to the center of the well (or vice versa) in a quarter vibrational period, less than the half-period required for motion from the inner wall to the outer wall. Therefore, a pulse tuned to the absorption maximum must be shorter than a pulse tuned to the edge of the spectrum to prevent the wavepacket from being washed out by movement during the pulse. Since the requirement for a more narrow frequency spectrum and the requirement for a shorter pulse are contradictory, the pump–probe signals have smaller vibrational modulation depth for a pump pulse tuned to the center of the well, as seen in Figure 8. In cases where the slope of the difference potential is very small, pulses which are vibrationally abrupt may be resonant with large portions of the range of thermally populated coordinates, virtually eliminating the vibrational modulation of the pump–probe signal for pulses tuned to the center of the well.

In general, the classical picture predicts that the optimum pump pulse duration will be different for the ground and excited state wavepackets for two reasons: (1) The relevant potential which determines how motion during the pulse influences the width of the wavepacket is the excited state potential, not the ground state potential. (2) The yardstick for covering too wide a range of coordinates has shifted from the ground state thermal equilibrium phase space distribution to any excited state distribution in a vibrational quasi-equilibrium, since an excited state phase space distribution in vibrational quasi-equilibrium does not oscillate. In particular, the classical theory suggests that a $\delta$ function pulse which replicates the ground state equilibrium distribution may not produce the most narrow excited state wavepacket. Near the turning points, the ground state wavepackets created at room temperature by a 30 fs pulse centered at 580 are more narrow in coordinate space than the $v = 0$ probability distribution (compare the hole in Figure 5 with the half-maxima of $\psi^2$ for the zero-point level separated by 0.085 Å). Once the pulse is short enough to prevent too much motion on the excited state surface during the pulse, we expect the excited state wavepacket width to be about the same width as that of the ground state hole (i.e., nearly equal and opposite wavepackets), although the optimum pulse duration may be different. According to the classical theory, the optimum pulse duration should also decrease with increasing temperature.

The optimum probe pulse duration for sharp pump–probe signals can differ from the optimum pump pulse duration if different potentials (or different regions of the same potentials) are involved, as in femtosecond studies of chemical reactions. As the local slope of the difference potential drops, a given probe pulse spectrum samples a wider range of internuclear distances. This can smear out the signals even from sharp wavepackets. In the case of parallel surfaces (e.g. asymptotic reaction products), one merely detects a stepwise increase in the number of molecules in the probed range of coordinates, as observed by Rose, Rosker, and Zewail when using the sodium D line as a probe of NaI photodissociation dynamics.

The considerations above are for transform-limited pulses, and exceptions occur for chirped pulses, where the frequency sweep can be chosen to match the instantaneous electronic energy gap of a particular group of trajectories, allowing selection of both position and momentum. The use of chirped pulses to control chemical reactions was suggested as early as 1965. Recently, Wilson and co-workers have implemented optimal chirped pulse control of excited state vibrational wavepackets in $^1I_2$.

VIII. Discussion

VIII.A. Optical Forces. Using a quantum mechanical pulse propagator, Cina and Smith have shown that a resonant optical pulse provides a momentum impulse to the ground state which initially moves the ground state density matrix $\rho_g$ toward greater electronic energy gaps. This resonant momentum impulse is opposite in direction to the momentum imparted by an off-
resonant pulse and is proportional to the intensity of the optical pulse for fixed pulse duration. It can be shown \(^{36}\) that this resonant momentum impulse has a classical limit \(^{38}\) which is related to the off-resonant impulsive stimulated Raman scattering effect studied by Nelson and co-workers.\(^{14}\) As noted by Smith, Ungar, and Cina,\(^{24}\) an important facet of the resonant optical force is that we can regard the momentum as imparted to the hole \(\delta Q_h\) (this follows trivially from \(\delta Q_h = \delta Q_{EO} + \delta Q_e\), \(\langle p \rangle = \text{tr}(\delta Q_{EO})\), and \(\langle \delta Q_{EO} \rangle = \text{tr}(\delta Q_{EO}^2) = 0\)). We note that since both \(\langle p \rangle\) and \(\text{tr}(\delta Q_{EO})\) are proportional to \(E^2\) in the weak field limit, the ratio \(\langle p \rangle/\text{tr}(\delta Q_e)\), which gives the momentum density of the hole, is independent of intensity in the weak field limit. Because the hole is mainly a negative operator, it moves toward smaller electronic energy gaps in the resonance region. In the classical picture of section III, the momentum imparted to the hole displaces \(\delta Q_h\) vertically along the momentum axis. Therefore, the hole moves from side to side even if it is created at the exact center of the ground state well, where one might expect only expansion and contraction. Figure 5 of the paper by Smith, Ungar, and Cina\(^{24}\) shows several snapshots of the side to side motion and spreading of \((R\delta Q_{EO}^\dagger R)\) created by a pump pulse which is classically resonant at the exact center of the 1G ground state well; the side to side motion caused by the optical force is also readily apparent in their calculations of iodine 521/539 and 521/503 pump–probe signals at 300 K (see Figure 4 of their paper). This is in contrast to the calculations shown above, where motion caused by the ground state potential dominates the form of the pump–probe signals.

VIII.B. Optical Bloch Equations. The first-order optical Bloch equations describe the exponential relaxation of the density matrix toward equilibrium or the decay of \(\delta Q_e\) to zero. In the optical Bloch limit, each contribution to the pump–probe signal can be expressed as a sum of decaying exponentials and exponentially damped cosines. For the excited state, \(\delta Q_e\) is a density matrix and obeys the density matrix inequalities\(^{35}\) \(Q_{ij}^{(\delta Q)} \geq |q_{ij}|^2\), from which we can obtain the inequality for the optical Bloch parameters \((1/T_{1\delta}) + (1/T_{2\delta}) \leq (2/T_{ij})\) describing the exponential lifetime \(T_{ij}\) of \(\delta Q_{ij}\). Each excited state signal can be written in the form

\[
S_{pp} = \sum_{(\tau,\rho)} A_{\tau\rho} \cos(\omega_T \tau + \phi_T) \exp(-\tau/T_{ij}) \tag{18}
\]

and the density matrix inequality \(Q_{ii}^{(\tau)} + Q_{ii}^{(\rho)} \geq |Q_{ii}^{(\tau)} + Q_{ii}^{(\rho)}|\) implies that \(|A_{\tau} + A_{\rho} \geq |A_{\tau}|\) from the form of the pump–probe signal in eq 8. One can also derive further inequalities, but the essential point is that each signal is separately signed and does not pass through zero (a result which does not depend on the optical Bloch equations). For the ground state, even if \(\delta Q_h\) is negative (a hole), \(\delta Q_e\) is not the ground state density matrix, and we cannot rigorously apply the density matrix inequality to obtain relationships between the exponential lifetimes \(T_{ij}\) of the elements \(\delta Q_{ij}\). Violations of the inequality \((1/T_{1\delta}) + (1/T_{2\delta}) \leq (2/T_{ij})\) for certain bath models have been discussed by Skinner and others,\(^{69}\) but not yet experimentally observed. The inequality \(|A_{\tau} + A_{\rho} \geq |A_{\tau}|\) and others for \(A_{\tau}\) hold rigorously whenever \(\delta Q_h\) is negative. The nonrigorous inequalities for \(T_{ij}\) can be very useful because the sign of the pure exponential term \(A_{\tau}\) is the sign of the signal. Because nearby vibrational levels of the same electronic state will often have similar lifetimes, the magnitude of \(T_{ij}\) restricts the damped cosine terms which can be part of the same signal to those with smaller or equal \(T_{ij}\). This grouping of exponential and oscillatory terms can eliminate the ambiguity between a sign change and a 180° phase shift. For examples of the application of these inequalities, see Scherer, Jonas, and Fleming.\(^{8}\)

VIII.C. Absorption or Raman? In discussing the ground state hole classically, we have not mentioned Raman scattering explicitly, yet a moving ground state hole clearly requires that the optical pulse create quantum mechanical superposition states by Raman scattering. There seems to be a contradiction between the classical picture of localized absorption and the quantum picture of absorption plus stimulated Raman scattering. Actually, the two viewpoints are not contradictory, but correspond to complementary views of the same system through different ensembles with the same density matrix. An ensemble is specified by giving a set of states \(\psi\) (not necessarily eigenstates) and their probabilities \(p_{\psi}\). In terms of the density operator, the expectation value \(\langle M\rangle\) of an operator \(M\) is given by \(\langle M\rangle = \text{tr}(g(M))\), where \(\text{tr}\) denotes the trace (i.e. sum of diagonal matrix elements). The time evolution of the density matrix is given by \(g(t) = U(t) g(0) U^\dagger(t)\), where \(U(t)\) is the propagator. After a measurement of an operator with eigenvectors \(\phi\), the new density operator is \(g' = \Sigma \langle \phi | \phi \rangle (\phi) / (\phi)\). From these three statements, it is clear that two ensembles with the same density matrix have the same observable properties and cannot be experimentally distinguished even if the probabilities \(p_{\psi}\) and states \(\psi\) in the two ensembles are different. We call ensembles with the same density operator equivalent ensembles. As illustrated by the following simple example, absorption and resonant stimulated Raman scattering are very closely related.

Let us consider a system with a symmetric double-well electronic ground state and an excited electronic state with a single potential well nearly identical to the ground state well on the left. The two lowest eigenstates of the ground state (labeled \(|s\rangle\) for symmetric and \(|a\rangle\) for antisymmetric) are equally populated, but all other levels are unpopulated. This system can be represented by the ensemble \(p_s = 1/2, p_a = 1/2\). In the eigenstate basis, this ensemble has density matrix elements \(|s\rangle \langle s| = \langle a|\langle a|\) = 1/2 and \(|s\rangle \langle a| = |a\rangle \langle s| = 0\). The effect of a short (compared to the inverse tunneling splitting) electronically resonant pulse may be calculated from the (interaction picture) second-order pump propagator\(^{39}\) \([I - ie(1/2)\epsilon^2], where \(\epsilon = \mu E T_{h}\).

\[
|s\rangle \rightarrow |\phi_s\rangle = (1 - (1/2)\epsilon^2)|s\rangle - (1/2)\epsilon|a\rangle - ie|e\rangle
\]

\[
|a\rangle \rightarrow |\phi_a\rangle = (1 - (1/2)\epsilon^2)|a\rangle - (1/2)\epsilon|s\rangle - ie|e\rangle
\]

After the pulse, the density matrix has reduced diagonal elements and a nonzero off-diagonal element between the states \(|s\rangle\) and \(|a\rangle\). This looks like a combination of both absorption and resonant stimulated Raman scattering.

We can also consider the ensemble composed of two time dependent states which happen to be localized in the left and right wells at the time of the optical pulse. We have \(p_s = 1/2\) and \(p_a = 1/2\), where \(|L\rangle = (|s\rangle + |a\rangle)/\sqrt{2}\) and \(|R\rangle = (|s\rangle - |a\rangle)/\sqrt{2}\). In the eigenstate basis, this ensemble has the same density matrix as the ensemble used above (viz., \(|s\rangle \langle s| = \langle a|\langle a| = 1/2\) and \(|s\rangle \langle a| = |a\rangle \langle s| = 0\), so the two ensembles are equivalent and physically indistinguishable. However, it is clear that only the state \(|L\rangle\) absorbs light, while \(|R\rangle\) is not coupled to the optical field at all. The second-order effect of the pulse may be calculated from the infinitesimal pump propagator and the definitions of the states \(|L\rangle\) and \(|R\rangle\):

\[
|L\rangle \rightarrow |\phi_L\rangle = (1 - \epsilon^2)|L\rangle - \sqrt{2}ie|e\rangle
\]

\[
|R\rangle \rightarrow |\phi_R\rangle = |R\rangle
\]

It appears that the absorption of the pulse has created a hole in the left-hand well. It is easy to verify that the density ma-
Femtosecond Wavepacket Spectroscopy

The wavepackets generated by a vibrationally abrupt pump pulse are readily visualized with $\delta Q_\beta$, the change in the density matrix caused by the pump. It must be emphasized that both ground and excited state wavepacket creations are weak optical field effects which are proportional to the intensity of the pulse in the weak field limit. $\delta Q_\beta$ provides a natural definition of the ground state wavepacket: identification of $\delta Q_\beta$ with the ground state wavepacket is useful because, as we have shown, the change in absorption by the ground state may be calculated from $\delta Q_\beta$ alone; this definition also corresponds to the change in the classical phase space density and allows one to easily visualize oscillation and spreading; at high temperatures $\delta Q_\beta$ becomes a narrow pure hole (i.e. a density like negative operator) which moves and spreads in a classical way for short times. $\delta Q_\beta$, the excited state wavepacket, also moves and spreads in a classical fashion for short times if the temperature is high. Although thermal averaging smooths the complex pump–probe signals calculated at low temperature toward the classical limit as temperature is increased, the signals at low temperature have maxima and dominant frequencies which roughly match classical expectations.

The classical picture leads one to expect that the typical two-color pump–probe signal contains at least the first and second harmonics of the vibrational frequency: both frequencies are required to produce narrow peaks or the sort of doublets in the pump–probe signal which result from probing a wavepacket in between its turning point and the center of the well. Third and higher harmonics can help to produce sharp or broad maxima in the pump–probe signals (the 30 fs pulse duration used in these simulations effectively discriminates against the third and higher harmonics because the frequency bandwidth is too narrow).

The dominant frequency is double the vibrational frequency near the absorption maximum, which creates wavepackets (or probes them) at the center of the well. Despite correctly explained observations of doubled excited state frequencies by four experimental groups,\(^5,^6,^8,^12,^13\) this does not seem to be widely appreciated. In the early studies, the beat frequencies in the femtosecond pump–probe studies were compared to the off-resonant Raman spectrum,\(^1,^2,^7\) which contains only vibrational fundamentals. As emphasized by Pollard, Mathies, and co-workers, a more appropriate comparison would be to the resonance Raman spectrum,\(^1,^7,^8\) where overtones of highly displaced modes commonly appear. The electronic change in equilibrium geometry must be greater than the vibrational displacement at the classical turning points of the zero-point level for second harmonics of the vibrational frequencies to dominate, but this happens for some vibrations even in large molecules. The vibrational modes with the largest displacements should dominate the femtosecond pump–probe experiments if the pulses are vibrationally abrupt with respect to those modes. It is important to recognize that doubled frequencies can appear in both ground and excited state signals (doubled frequencies have been observed in both the X and B states of I\(^8\)) and that the problem of doubled ground state frequencies is worst for the easiest experiments: single-color pump–probe spectroscopy with the wavelength set at the absorption maximum.

Excited state wavepackets can be used to study vibrations which are obscured in the frequency domain by inhomogeneous broadening in solution as well as electronic curve crossing, isomerization, and dissociation. In principle, the pump–probe signals from ground state wavepackets provide information similar to that obtained from frequency domain resonance Raman spectroscopy. For high-frequency vibrations of stable molecules, the signal from a ground state wavepacket is likely to be simply a nuisance which must be eliminated in order to interpret excited state wavepacket signals. For low-frequency vibrations (where the vibrational Raman shift may be obscured by scattered light)\(^2\) and unstable molecules (where the Raman spectrum may not have been observed)\(^7\) the signal from ground state wavepackets can most easily provide information which is otherwise unavailable.

Acknowledgment. We thank Professor Clyde A. Hutchison Jr. for instructive discussions about the density operator and Jeff Cina, Timothy Smith, and Lowell Ungar for useful discussions and for sharing their results prior to publication. D.M.J. thanks the NSF for a postdoctoral fellowship. This work was supported by the Petroleum Research Fund and the National Science Foundation.

References and Notes

(11) We use the term wavepackets somewhat loosely to refer to coherent mixtures represented by a density matrix. Note that the concept of a "pure hole" is totally unrelated to the concept of a density matrix representing a "pure" rather than "mixed" state.
Excited state signal at the \( B \) state frequency which is first observed after about 100 fs delay.

These transient dichroism signals are signed if the rotational motion is diffusive so that rotational alignment recurrences (see: Felker, P. M. J. Phys. Chem. 1992, 96, 7844–7857) with alignment perpendicular to the initial alignment are impossible.

If every Hermitian operator represents an observable, as is often assumed in quantum mechanics, then inequality 14 is true if and only if inequality 16 holds.

- Reference 17 reported that the stimulated emission contribution to the calculated differential transmittance spectrum shifted from the 250 cm\(^{-1}\) frequency as it crossed the center of the well, but erroneously ascribed the initial alignment are impossible.

The opposite momentum impulse can be derived from the optical force \( F = -\nabla \Delta U = \nabla (1/2)\alpha' E(t')^2 \) arising from the average change in energy of a dielectric material in an electromagnetic field \( \Delta U = -pE \).

For example, dynamic absorption could detect a Raman scattering exchange of blue probe photons for red ones without any change in total photon number.

\[ \Delta \mu = 2 \sqrt{2} \sqrt{2} \]