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13. ABSTRACT (Maximum 200 words)

Considerable progress has been made in the two main (and interrelated) areas in which the recent research has been focussed. These are (a) the development of novel, intense, femtosecond-time-scale, VUV laser sources, and (b) the development of femtosecond-time-scale, transition-state absorption spectroscopy of photodissociating gas-phase molecules. In both of these areas, some trails have been blazed that will undoubtedly soon be followed by others. A third area of investigation was to examine the possibility of two-photon amplification in the molecular system diphenyl hexatriene (DPH). Here the critical experiment still remains to be done. However, researchers were able to show that DPH does satisfy one stringent requirement for a potential two-photon amplifying system, namely, that it be completely stable against one-photon lasing under conditions of very heavy optical pumping.

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Femtosecond Laser Studies of Excited State Dynamics

FINAL REPORT

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1. Introduction

During the past three years (the reporting period of contract DAAL03-90-C-0006) we feel that considerable progress has been made by our group in the two main (and interrelated) areas in which our recent research has been focussed. These are (a) the development of novel, intense, femtosecond-time-scale, VUV laser sources, and (b) the development of femtosecond-time-scale, transition-state absorption spectroscopy of photodissociating gas-phase molecules. In both of these areas, we feel that we have blazed some trails that will undoubtedly soon be followed by others. A third area of investigation suggested in our original proposal was to examine the possibility of two-photon amplification in the molecular system diphenyl hexatriene (DPH). Here, we must report, the critical experiment still remains to be done. However, we recently were able to show that DPH does satisfy one stringent requirement for a potential two-photon amplifying system, namely, that it be completely stable against one-photon lasing under conditions of very heavy optical pumping.

2. Generation of Tunable, Femtosecond-Time-Scale, VUV Pulses by Four-Wave, Difference-Frequency Mixing in Xenon

It is well known that two primary laser beams at frequencies ω_1, ω_2 can be combined in a non-linear mixing crystal to generate an output beam at the sum-frequency $\omega_3 = \omega_1 + \omega_2$, provided that the wavelength λ_3 is, roughly speaking, greater than $\simeq 200$ nm. At shorter wavelengths, severe problems arise, associated both with the limited VUV transmission of crystalline materials, and with the limited extent to which three-wave mixing processes that result in VUV output can be phase-matched. It has long been recognized that with the use of a higher-order non-linear process, *four-wave difference-frequency mixing ($\omega_3 = 2\omega_1 - \omega_2$) in gases*, one is no longer prevented by the two above-mentioned effects from generating coherent light at wavelengths shorter than 200 nm. However, the reported conversion efficiencies have generally been in the $10^{-5} - 10^{-6}$ range. In a recent investigation[1], performed under the just concluded AROD contract by our group, femtosecond-time-scale VUV pulses were generated by the second method discussed above. For the input beam at ω_1, 180-fsec, 308-nm pulses that had been amplified in a standard XeCl-discharge excimer gain module were employed. For the input beam at ω_2, near-IR pulses (pulsewidth 150 fsec, energy 150 μJ, wavelength $\simeq 757$ nm) were used. The input beam wavelength λ_2 was chosen so that the output beam wavelength λ_3 would be at 193 nm, i.e., at the ArF excimer wavelength. The mixing medium employed was 1 atm. of Xe gas.

Femtosecond-time-scale pulses at $\simeq 193$ nm with energies in the 0.25-μJ range were produced at the output window of the Xe cell. The energies of the pulses produced were thus about 10^{-3} of the pulse energies applied at ω_2. (This ob-

served improvement in four-wave mixing conversion efficiency over values previously reported can be largely attributed to the fact that we used femtosecond-time-scale pulses for the beams at ω_1 and ω_2.) It was, furthermore, observed that the output pulses could be tuned over $\simeq 1,800$ cm^{-1} simply by changing the *relative delay* between the input pulses, a result of the combined effects of self-phase modulation and group velocity dispersion occurring in the beam at ω_1 as it passed through various optical components before entering the Xe cell. By tuning these pulses to the maximum of the ArF gain profile, and then double-passing them in a standard ArF-discharge excimer gain module, we were able to produce $\simeq 300$-fsec, $\simeq 300$-μJ pulses at 193 nm.

The specific input beam frequencies utilized in the above-described $2\omega_1 - \omega_2$ four-wave mixing scheme were chosen on the basis of immediate convenience, and did not result from considerations related to optimization of the conversion efficiency. Indeed, none of the pulses, input or output, were resonant with energy levels of Xe in the actual scheme used. The situation becomes entirely different when the beam at ω_1 is chosen to be a femtosecond-time-scale pulse at $\simeq 248.5$ nm, the wavelength of the KrF excimer. There is an allowed two-photon resonance in Xe at 80,119 cm^{-1} (see Fig. 1) that enormously enhances the non-linear susceptibility when λ_1 is chosen to be $\simeq 248.5$ nm. In Fig. 2 this enhancement is illustrated through a comparison of $I_3(v)$ plots recorded at the two output wavelengths at which it is possible to generate light by four-wave difference-frequency mixing with input beams at 308 nm and 248.5 nm. Results are shown for mixing in both Xe and Kr. Resonance enhancement is seen to occur only in Xe, and only for the case $\lambda_1 = 248.5$ nm, $\lambda_2 = 308$ nm, not the reverse. The resonance enhancement appears to enhance the conversion efficiency by almost two orders of magnitude. From this result, and from the fact that $\simeq 0.25$-μJ pulses were produced in our 193-nm four-wave difference-frequency mixing experiment, one can reasonably extrapolate that, with the use of KrF-amplified ultrashort pulses for the beam at ω_1, and with the use of dye-amplified continuum pulses for the beam at ω_2, *one should be able to generate (in Xe gas) femtosecond-time-scale VUV pulses at the few-tens-of-microjoules energy level, tunable anywhere between 150 and 200 nm.* It is of particular interest to our own group (see Sec. 3) that such a source already has sufficient energy to photodissociate enough VUV-absorbing gas-phase molecules to allow transition-state absorption spectroscopy to be performed on the resulting fragments.

Before describing our most recent experiment dealing with the generation of VUV femtosecond-time-scale pulses, let us consider some of the favorable characteristics of the four-wave difference-frequency mixing scheme described above. Reliance upon KrF-excimer amplification to produce the required femtosecond-time-scale pulses at ω_1 should be viewed positively, since already several years ago the Göttingen group of Professor F.P. Schäfer demonstrated that with KrF amplifiers one can produce pulses at 248.5 nm with good spatial beam quality having pulse widths as short as 60 fsec and pulse

ent gies in the few-tens-of-mJ range. As far as the (visible) beam at ω_2 is concerned, this can ideally be provided by near-threshold continuum generation, post-amplification in prism dye cells, and subsequent temporal pulse compression via a prism pair. With the use of such techniques, several groups have reported the generation of energetic visible pulses with pulse durations in the 20-fsec range. The pulsewidth of the generated VUV pulse at ω_3 ideally should approximate the shorter of the two input pulsewidths. The mixing medium (a few Torr of Xe) is completely transparent in the range 150-200 nm. Furthermore, it cannot be permanently damaged by the focussing of the input pulses.

With use of the specific four-wave mixing scheme described above to prepare VUV femtosecond-time-scale seed pulses, one should now be able to determine how well various VUV amplifiers that are known to work on the nanosecond-time-scale will operate as amplifiers of femtosecond-time-scale pulses. Two such systems readily come to mind. These are (1) the discharge-pumped F_2^* amplifier at 157.5 nm, and (2) the Xe_2^* amplifier at 172 nm. The former has recently been commercially developed (Lambda-Physik GmbH, LPF 205 VUV Excimer Laser) into a powerful (150 mJ/pulse), nanosecond-time-scale, laser. The latter has, to our knowledge, only successfully been operated as an e-beam-pumped laser, although Grieneisen et al.[2] have suggested that it can be efficiently excited by optical pumping with an F_2 laser - and it is this means of excitation that was considered in our recent proposal[1] to test the system as an ultrafast amplifier. Because the F_2 gain medium is experimentally simpler to excite, we have chosen to initially concentrate our laboratory efforts in trying to prepare femtosecond-time-scale seed pulses that would be suitable for testing this system as an ultrafast pulse amplifier.

As a preliminary step towards generating seed pulses at the desired 157.5-nm wavelength, our group has very recently[3] generated femtosecond-time-scale pulses at 155.6 nm by four-wave difference-frequency mixing in Xe. using 300-fsec, 248.5-nm pulses for the beam at λ_1 and ultrashort light pulses at 616 nm for the beam at λ_2. (In our laboratory, femtosecond-time-scale pulses at various needed wavelengths have been generally produced with use of the following basic scheme: dye-amplification of CPM laser pulses (616 nm) → frequency-doubling (308 nm) → amplification in XeCl (308 nm) → continuum generation in high-pressure argon (broadband UV) → amplification in KrF (248.5 nm). Thus, $\simeq$100-fsec pulses at 616 nm with relatively good beam quality are readily available to us. The $\simeq$300-fsec pulses we obtain at 248.5 nm as KrF-amplified continuum pulses are energetic ($\simeq$4mJ), but they appear to be spatially comprised of micro-filaments and are consequently not as focussable as are our amplified pulses at 616 and 308 nm. For example, with our 248.5-nm pulses we cannot generate continua in rare gases, as reported in Ref 4.)

With $\simeq$3-mJ pulses at λ_1, and $\simeq$150-μJ pulses at λ_2 coaxially focussed with a 25-cm lens into an optimal Xe pressure of $\simeq$10 Torr, $\simeq$4-μJ pulses of $\simeq$155.6 nm radiation were measured with a pyroelectric laser energy meter when the input pulses were made temporally coincident[3]. *An $\omega_2 \rightarrow \omega_3$ conversion efficiency of several percent was thus achieved,* even with use of a driving beam at ω_1 having less-than-optimal spatial coherence properties. The measured 4-μJ output pulse energy is in a good range for making convenient single-pass measurements of the short-pulse amplification coefficient in a typical F_2 discharge. However, *in a very recent measurement we have found that at 155.6 nm there appears to be virtually no short-pulse gain in the F_2 system.* (We used a standard excimer gain module with a 40-cm-long discharge length, modified by the installation of more-closely-spaced electrodes. The (He) buffer gas pressure was 4 bars, limited by the mechanical strength of the gain module.) We are thus compelled to make the effort to generate (by the method outlined earlier in this section) the correct λ_3 wavelength (157.5 nm) for maximum F_2 gain. This effort is currently underway. A comparison of the short-pulse (unknown) and long-pulse (known) F_2 gain coefficients at 157.5 nm should provide considerable insight into the gain dynamics of this largely unexplored, but highly interesting, amplifying medium.

3. Kinetic Absorption Spectroscopy of Interacting Fragments Produced by the Femtosecond-Time-Scale Photodissociation of Gas-Phase Molecules

Under Contract DAAL03-90-C-0003 we have continued to develop both new experimental techniques and new theory for the study, by kinetic absorption spectroscopy, of fragments which are directly formed by the photodissociation of gas-phase molecules. *These fragments are observed during the first picosecond or so of their existence, that is, while they are still subject to the force fields of one another.* Initial development of this field occurred under our previous AROD Contract DAAL03-86-C0008.

Figure 3 shows typical transient absorption spectra that we were able to obtain shortly after the beginning of the current AROD contract[5]. Due to an improved optical layout, both the spectral resolution and signal-to-noise are considerably better than what we had obtained previously. Almost 2π radians of "accumulated phase" (Refs. 5, 6, and 7) are recorded at the shortest pump-probe delay times. In Fig. 4 are shown recently obtained spectra for the GaCl system[8]. The signal-to-noise ratio here shows still more improvement, which we attribute to a more stable optical layout (between the data-taking times corresponding to Figs. 3 and 4, our laboratory was equipped with a new optical bench system), a new OMA system, and somewhat more averaging. In addition, we have recently improved the amplitude stability of our dye amplifier chain by incorporating a diode-pumped seeder into the Nd:YAG pump laser. However, since we installed the seeder we have not had the opportunity to

take new transient absorption spectra to know exactly how much benefit was gained from having taken this step.

From a theoretical standpoint, we have gained a much deeper understanding about the lineshapes of the transient absorption spectra which we observe. Our most complete theoretical treatment was published in 1991 (ref. 6). Condensed versions of the theory appear in Refs. 5 and 7. In Ref. 7 some striking additional physical insights are presented. An example of the theory being applied is shown in Fig. 5 (taken from Ref. 7). Figure 5 shows calculated $T\ell$ spectra for conditions that are generally similar to those that apply in the case of Fig. 3 (only the specific $T\ell$ transitions shown being probed are different). Note that all the main striking features of the observed spectra in the so-called "impact spectral region", that is, in the spectral region within a few cm^{-1} of the free atom resonance are effectively captured by the theoretical modeling.

Our approach to transition-state spectroscopy of photodissociating gas-phase molecules relies upon transmission of probe light through the photodissociating sample, whereas the approach of A.H. Zewail's CalTech group relies upon fluorescence detection. Transmission measurements are inherently phase-sensitive, whereas fluorescence detection is sensitive only to the net population excited by a femtosecond-time-scale probe pulse. A consequence of this is that in absorption studies one can examine the transient spectra to see how *both* the *amplitude* and *effective phase-shift* develop in time. From the combined use of these two measurements one can obtain important information about the dynamics of the photodissociating system. The power of this approach is nicely demonstrated in our recent GaCℓ study[8]. *Solely by analysis of the growth curves of the Ga-atom absorption features (two exit channels were found to be activated by 248.5-nm photolysis) and the time variations of the effective phase-shifts (both quantitities are automatically recorded in the transmission measurement and, hence, are directly recoverable by inspection of the spectra), we were able to specify the exact amount of kinetic energy released in the photodissociation process, as well as the precise spin-orbit quantum numbers of both atoms (i.e., Ga and Cℓ) produced in each exit channel.* These measurements provided a significantly corrected value for the dissociation energy of GaCℓ.

Summarizing this section: During the contract just concluded, we improved upon the techniques we had originally developed for recording "transition-state" absorption spectra of fragments produced by photodissociation of gas-phase molecules. The development of new femtosecond-time-scale VUV photolysis sources, discussed in the previous section, allows a much wider class of gas-phase molecules to be studied with this technique. The understanding that was gained of the factors that determine the "impact region" lineshapes of the transient absorption spectra observed in these experiments now enables one to obtain *from inspection of the spectra alone* kinetic information that would normally require the use of a separate time-of-flight appa-

ratus and/or laser Doppler velocitometry. Information about the potential energy curves (i.e., difference potentials) in the van der Waals region can also be obtained by such time-domain transmission measurements.

4. Towards a DPH Two-Photon Amplifier

As stated in the Introduction, during the just terminated AROD Contract we did make one concrete step towards a full assessment of the potential for diphenyl hexatriene (DPH) to be used as a two-photon, femtosecond-time-scale amplifier. (Our original Proposal for the just terminated AROD Contract contains a lengthy discussion of the basic ideas and considerations involved. These will not be repeated here.)

We studied DPH in the solvent methyl cyclohexane, in which it is very soluble. Also, the energy splitting between the DPH $1B_u$ and $2A_g$ states is still relatively large in this solvent. We pumped a thin quartz cuvette filled with DPH solution with $\simeq 200 mJ/cm^2$ of third-harmonic light (355 nm) from a Nd:YAG Q-switched laser. The pump light became fully absorbed in a few millimeters. (The 355-nm wavelength is just above the origin of the very intense $1B_u \leftarrow 1A_g$ absorption band. It is an ideal wavelength at which to pump the system.) *We observed the blue ($\simeq 440$-nm) $2A_g \rightarrow 1A_g$ fluorescence to decay with the same lifetime (13.5 nsec) that it does under mild excitation.* In other words, there is no one-photon $2A_g \rightarrow 1A_g$ lasing process to deplete the energy of the $2A_g$ state. The $2A_g$ excited-state absorption cross-section (at $\simeq 440$ nm), we now believe, is some 20 times the peak cross-section for gain in the blue! Thus, DPH in this solvent appears to be very stable against loss of stored energy via amplified spontaneous emission. It is possibly the case that one can store, say, 300 mJ of energy in a 1 cm^3 volume for 13.5 nsec, without any worry about feedback caused by ordinary Fresnel-type reflections from the flat surfaces of a polished 4-sided cuvette, or feedback caused by total internal reflections! It now becomes a *must* experiment to try to extract the stored energy via 2-photon stimulated emission in a multi-pass scheme. As we have earlier stated, this requires a femtosecond-time-scale "triggering" light pulse with a wavelength $\simeq 850$ nm, an energy $\simeq 1$ mJ, and a beam diameter $\simeq 1$ mm. Such pulses can be obtained from a Ti:sapphire-based oscillator/ chirped-pulse amplifier system, which we are currently constructing. Since the excited-state dynamics of DPH allows for a large, stable, $g \rightarrow g$, inversion, and since this experiment could possibly present unequivocal evidence for the existence of a two-photon amplifier, it should by all means be tried! We look forward to this exciting possibility.

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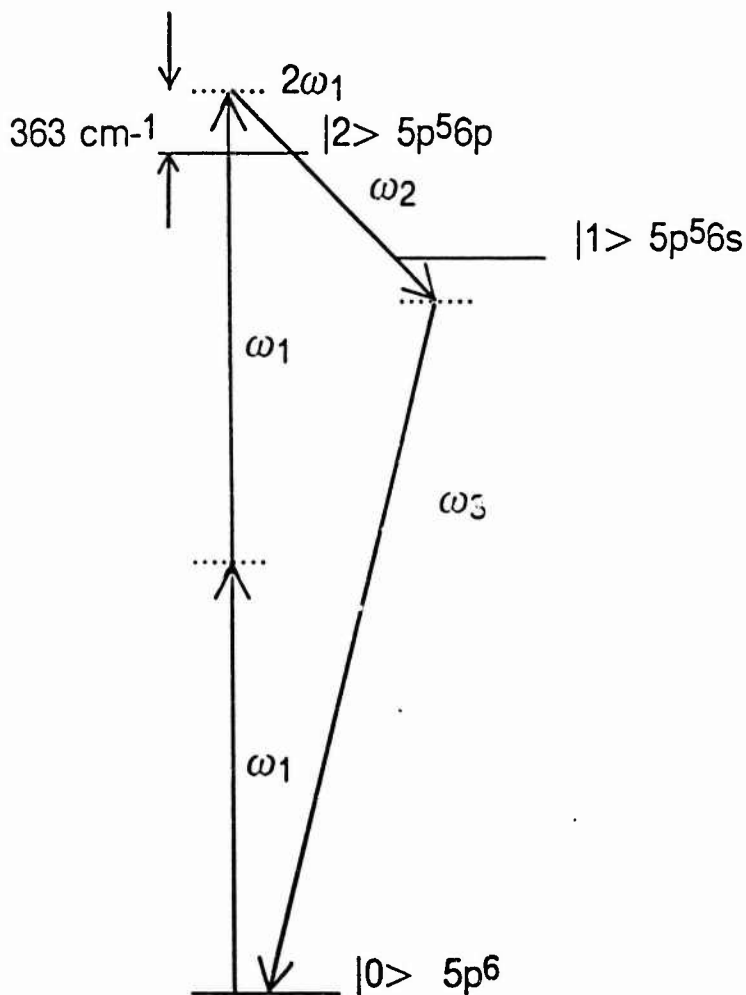
Figure 1. Resonantly-enhanced, four-wave, difference-frequency mixing scheme in Xe used for generation of femtosecond-time-scale VUV pulses. (After a figure in Ref. 3).
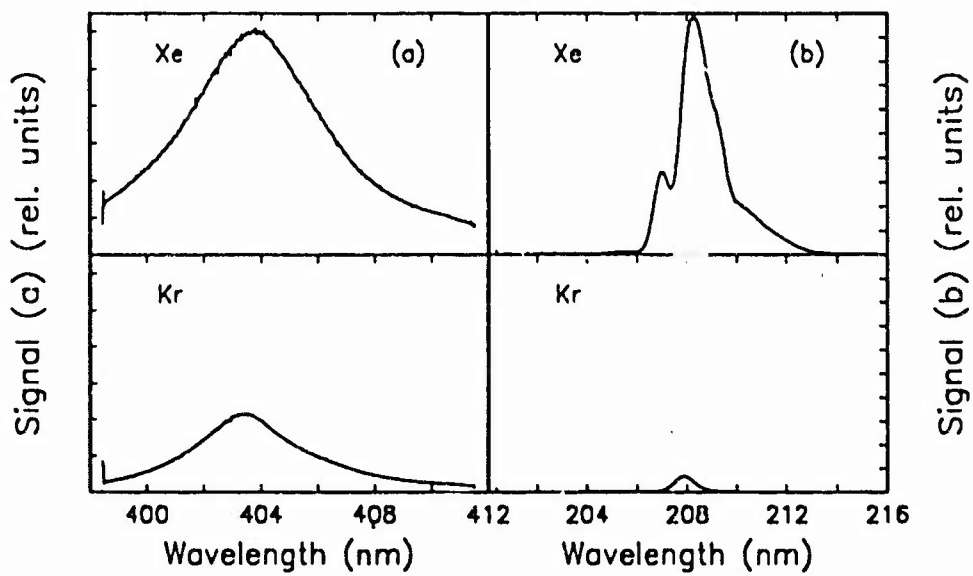
Figure 2. $I_3(\nu)$ plots showing effect of resonance enhancement of four-wave difference-frequency mixing in Xe with input beams at 248.5 and 308 nm. (After a figure in Ref. 3).
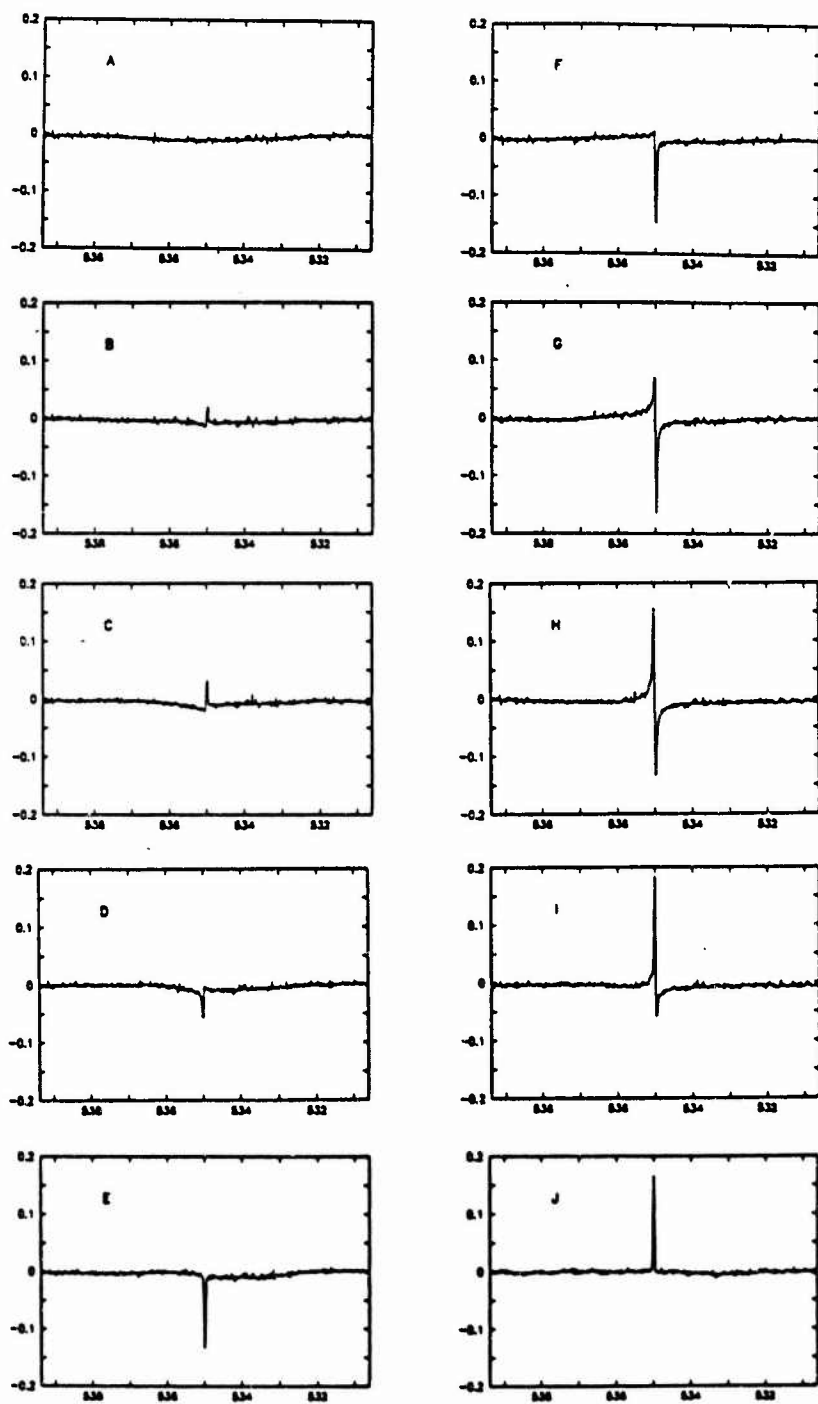
Figure 3. Transient absorption spectra taken in vicinity of 535-nm Tℓ resonance line following photolysis of TℓI vapor by 160-fsec, 308-nm pump pulses. Pump-probe delays increase with alphabetical designation. The maximum pump-probe delay shown here is about 1 psec. (After a figure in Ref. 5).
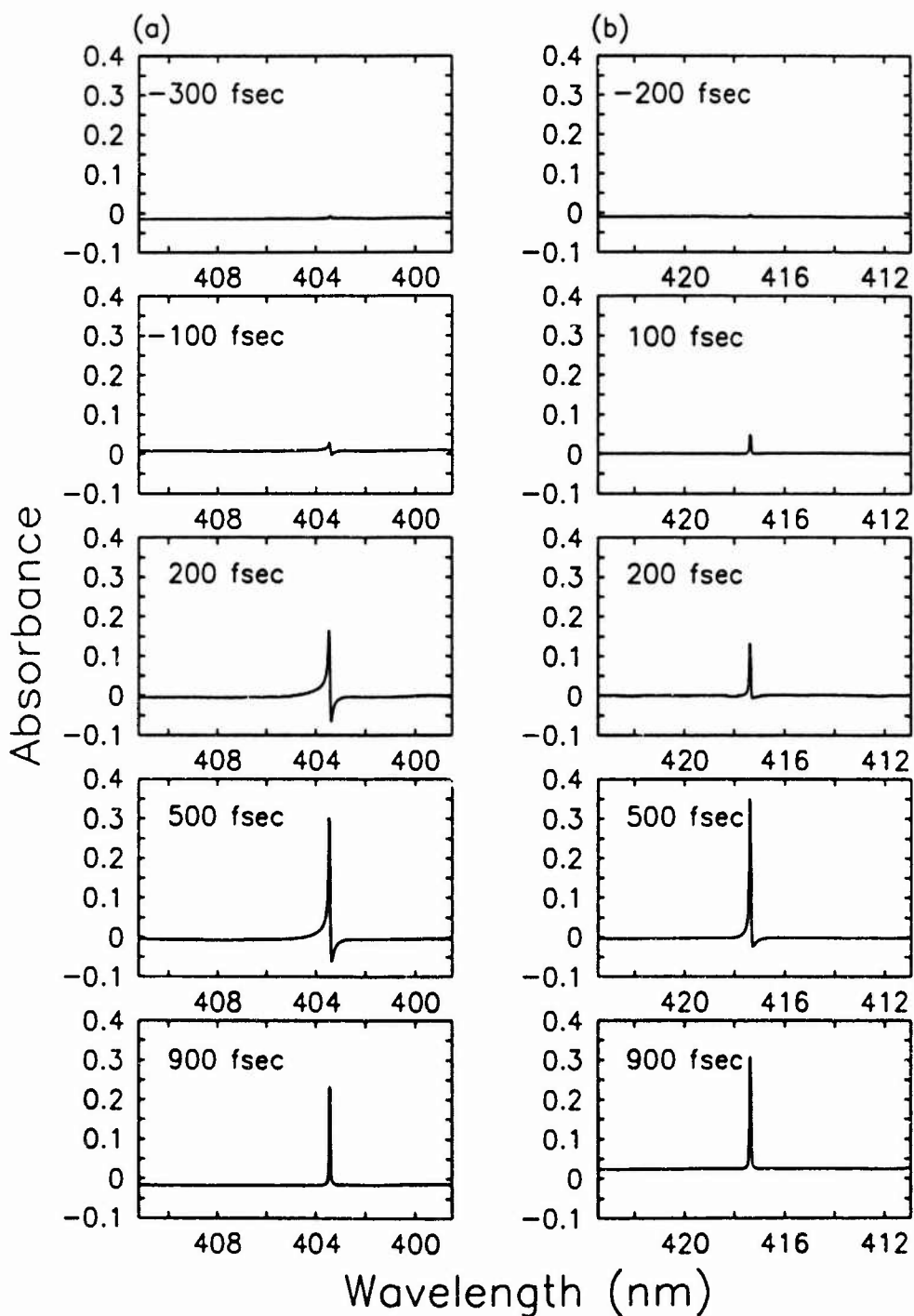
Figure 4. Examples of Ga-atom transient absorption spectra recorded for (a) 403.3-nm channel and (b) 417.2-nm channel. Absolute pump-probe delays are indicated. Data in (a) and (b) taken in consecutive runs on Ga, HCℓ mixture heated to $\simeq$230°C. (After a figure in Ref. 8).
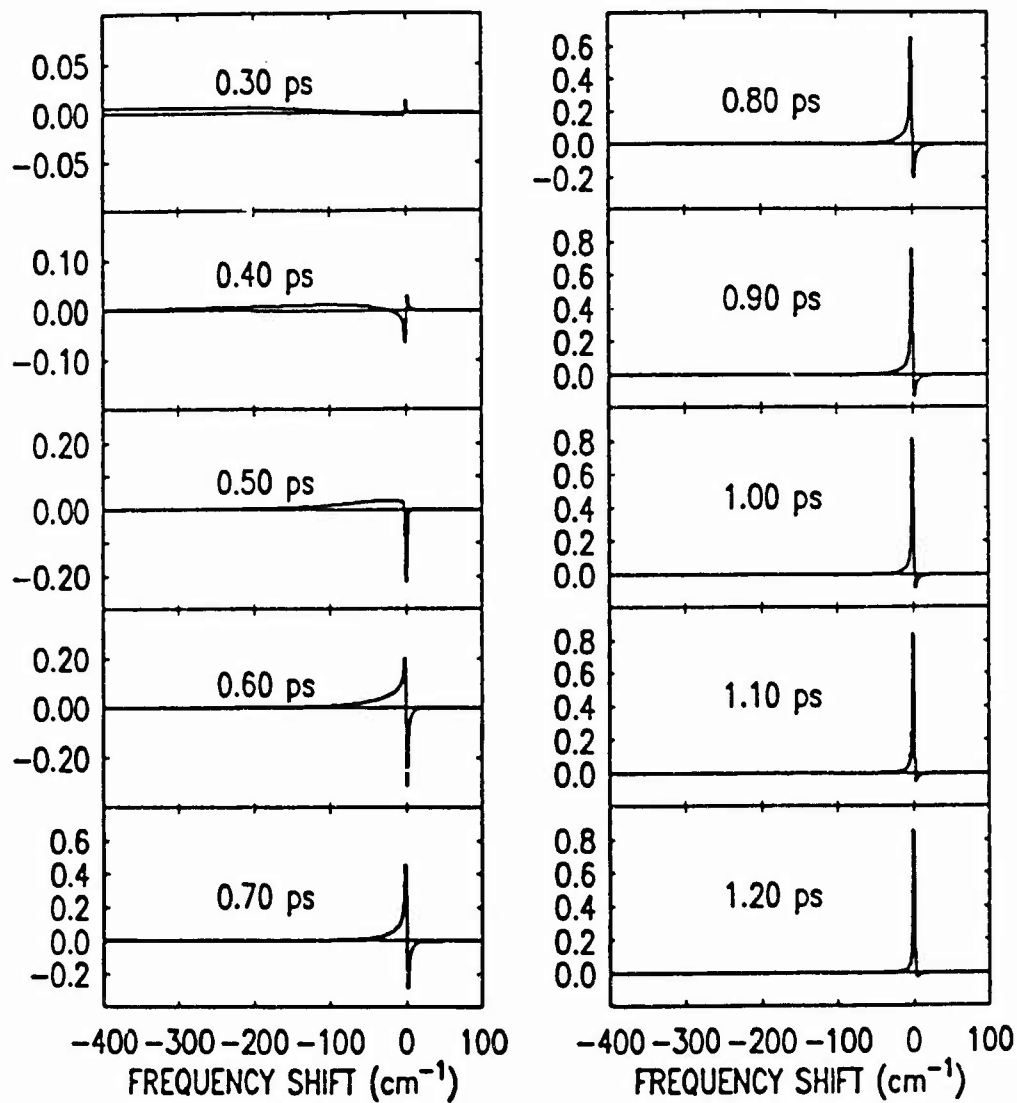
Figure 5. Calculated transmission spectra near the Tℓ 377.6 nm transition are shown for TℓI dissociated by a 160-fsec, 308-nm pump pulse. The calculations use a classical Fourier-transform approach with a full average over the ensemble of dissociating molecules. (After a figure in Ref. 7).