REFERENCES

1. Special issues of the Journal of the Optical Society of America B, Jan. 2, 1985; May 5, 1988: Optical Instabilities, R.W. Boyd, M.G. Raymer, and L.M. Narducci, eds., Cambridge, 1986.
2. J.P. Eckmann, Rev. Mod. Phys., 53, 643, 1981.
3. C.O. Weiss and J. Brock, Phys. Rev. Lett., 57, 2804,, 1986.
4. C.O. Weiss, N.B. Abraham and U. Huebner, Phys. Rev. Lett., to be published, 1988.
5. J.C. Antorantz and M.A. Rubio, J. Opt. Soc. Am. B, 5, 1070, 1988.
6. D. Hennequin, F. de Tomasi, B. Zambon and E. Arimondo, Phys. Rev. A., 37, 2243, 1988.
7. D. Dangoisse, A. Bekkali, F. Papoff, and P. Glorieux, Europhys. Lett., 6, 335, 1988.
8. F. T. Arecchi, A. Lapucci, R. Meucci, J. A. Roversi, and P. H. Coullet, Europhys. Lett, 6, 677 (1988).
9. F. Argoul, A. Arneodo, and P. Richetti, Phys. Lett. 120A, 269, 1987.
10. H. Haken, Phys. Lett., 53A, 77, 1975.

S P E C T R O S C O P Y

## SUBPICOSECOND UV KINETIC ABSORPTION SPECTROSCOPY

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R ecent advances in the generation of ultrashort laser pulses have made possible the investigation of chemical dynamics on a subpicosecond time scale, revealing details of the "transition states" region between reactants and products. For example, A.H. Zewail's group has reported subpicosecond laser-induced-fluorescence (LIF) studies of both directly dissociating[1] and predissociating[2] systems.

A recent focus of our group has been the development of a pump-probe apparatus capable of performing subpicosecond UV kinetic absorption spectroscopy experiments.[3,4] This apparatus has now been used to probe the formation of T_l atoms resulting from the subpicosecond UV (308, 248.5 nm) photolysis of T_lCl and T_lI vapors.[5] We observe unusual line shapes lasting for a period of roughly one picosecond, from the moment the atomic transition first appears to the point at which the final, asymptotic line shape is attained. We explain these spectra in terms of a model based upon the transient behavior of the radiating polarization induced by the probe continuum pulse as it interacts with the population of two-level atoms resulting from the photolysis pulse.

Figure 1(a) shows the appearance of time-resolved absorption spectra recorded in the viciniity of the 377.6-nm T_l $7S_{1/2} \leftarrow 6P_{1/2}$ resonance line, following the application of 160-fsec, 308-nm pump pulses to T_lI vapor. The absorbance was observed to be linear with pump intensity. It is seen that roughly one picosecond elapses from the moment the atomic transition appears to the point at which no further changes in the appearance of the atomic resonance line occur.

From previously reported time-of-flight data, one can deduce that the asymptotic line shape is reached before the T_l-I separation has increased by 7.1Å. This represents only an upper limit, since acceleration effects have been neglected. Note the existence of spectral regions of apparent negative absorption in Fig. 1(a). For the 351.9-nm, $6D_{5/2} \leftarrow 6P_{3/2}$ line, recorded under the same circumstances, this transient feature of apparent gain was absent, but a tran-
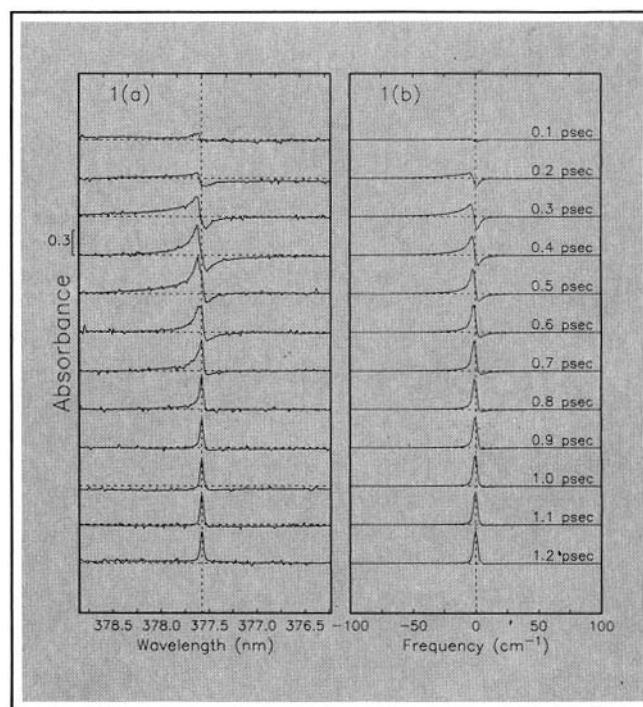
(a) Time-resolved absorption spectra recorded in the vicinity of the 377.6 nm T_l $7S_{1/2} \leftarrow 6P_{1/2}$ resonance line, following the application of 160-fsec, 308-nm pump pulses to T_lI vapor. The relative pump-probe separation is indicated on the right of (b). The horizontal dashed lines represent the absorption zero for each spectrum.
(b) Calculated transient absorption spectra.

sient asymmetry with a strong red wing was observed.[4] For T_1C1, with 248-nm excitation, the 351.9-nm absorption develops a pronounced transient blue wing.

Qualitatively, the apparent negative absorbance in Fig. 1(a) can be understood as the result of phase modulation of the probe continuum by the time-varying dispersion associated with a growing population of two-level atoms whose resonance frequencies shift in time. The shifts result from the fact that at early times in the dissociation, when the two atoms are close to one another, the atomic transition frequencies are perturbed by the bending of the potential energy curves that ultimately correlate with the atomic energy levels. The resulting phase modulation of the probe continuum simply redistributes the spectral energy of the latter, producing the regions of apparent negative absorption.

More quantitatively, one assumes that there are two contributions to the total output field emerging from the resonant vapor—the UV continuum probe pulse itself (assumed to occur at $t = 0$), and the field radiated by the polarization that the former induces in the vapor. The polarization is calculated from solutions to Schrödinger's equation for a two-level atom interacting with a continuum pulse. It is assumed that the photolytically produced atoms are formed in the ground state, with a time distribution that can be approximated by the pump pulse. Allowance is made for the existence of a continuous red (or blue) shift of the atomic transition frequency. The resultant expression for the time dependence of the induced polarization contains as a factor the phase integral exp contains as a factor the phase integral

$$\exp\left(\frac{-i}{\hbar}\int_0^t [\delta E_1(t') - \delta E_0(t')]dt'\right),$$

where the δE_i's denote the deviations of the upper and lower levels from their asymptotic values. This factor is the primary source of the asymmetry in the transient atomic absorption spectrum.

An example of a sequence of calculated spectra based upon this model is shown in Fig. 1(b). It is seen that a qualitative agreement exists between theory and experiment, with the particular feature of a transient spectral region of negative absorbance clearly displayed in the calculated spectra. Thus, the transient spectra we have obtained can be said to contain information regarding the "transition states" that occur between the time a molecule has absorbed a UV photon and the time its constituent atoms have fully separated. Specifically, information can be obtained about the frequency shifts that the atoms undergo during dissociation.

REFERENCES

1. M. Dantus, M.J. Rosker, and A.H. Zewail, J. Chem. Phys. 87, 2395 (1987).
2. M.J. Rosker, T.S. Rose, and A.H. Zewail, Chem. Phys. Lett. 146, 175 (1988).
3. J.H. Glownia, J. Misewich, and P.P. Sorokin, Chem Phys. Lett. 139, 491 (1987).
4. J.H. Glownia, J. Misewich, and P.P. Sorokin, in The Ultrafast Supercontinuum Laser Source, ed. by R.R. Alfano (Springer-Verlag, Berlin), in press.
5. J. Misewich, J.H. Glownia, J.E. Rothenberg, and P.P. Sorokin, Chem. Phys. Lett. 159, 374 (1988).
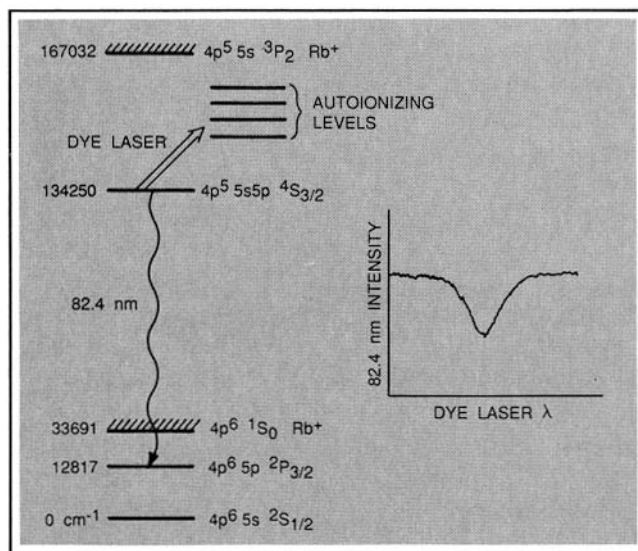
LASER DEPLETION SPECTROSCOPY

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Workers at Stanford have developed a new technique that allows the measurement of level positions, linewidths, autoionizing times, and transition oscillator strengths of core-excited levels, all to unprecedented accuracy.[1,2] Autoionizing lifetimes can be measured in the range of 10^{-9} to 10^{-14} sec, including lifetimes whose Lorentz width are far narrower than the Doppler or hyperfine width of the transition.

To perform depletion spectroscopy, a radiating core-excited level is used as a reference level from which to access the autoionizing manifold, as illustrated in the figure. The

Energy level diagram of Rb, showing the depletions spectroscopy technique.