CHEMPHYSCHEM

Bounce-by-Bounce Cavity Ring-Down Spectroscopy: Femtosecond Temporal Imaging**

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femtochemistry · femtosecond dynamics · kinetics · spectroscopy · temporal imaging

Cavity ring-down spectroscopy (CRDS) records the absorption spectrum of a species inside an optical cavity by measuring the change in the ring-down lifetime as a function of wavelength.[1–3] This technique is an advance over more traditional absorption methods because CRDS is free of interference caused by fluctuations in the light source. The principles of the technique are simple. For a linear optical cavity, two high reflectivity mirrors are placed opposite one another forming a stable optical resonator. A pulse of light enters the cavity through the back of one of the mirrors, bounces back and forth between the mirrors, and on each bounce some light emerges through the opposite mirror where it is detected. The losses of the cavity cause the intensity of the light to decrease exponentially[4] as a function of time, and the ring-down is characterized by a lifetime τ. For a typical 1-m cavity whose mirrors have a reflectivity of 99.99 %, the time between bounces on the same mirror (the "round-trip time") is 6 ns and the ring-down lifetime is 30 μs during which time the pulse has traveled a distance of 1 km. If a sample is placed inside the cavity that absorbs at the wavelength of the radiation, the absorption constitutes an additional loss and the resulting ring-down lifetime is shortened. Measurement of the variation of τ with wavelength produces the absorption spectrum. Typically, several ring-down profiles are averaged together and the analysis assumes the sample concentration does not change over the averaging time. We describe herein a variation on cavity ring-down spectroscopy, in which we record each pulse and use the comparison of one pulse to the next to remove light source fluctuations. This bounce-by-bounce technique is self-normalizing and allows us to probe the temporal variation in the sample concentration on the order of the round-trip time.

Bounce-by-bounce measurements require rapid detector response, which in the case of short cavities places a severe constraint on the detection dynamics. We describe the use of a time microscope[5–7] that gives the ability to follow dynamics on the subpicosecond timescale. Bounce-by-bounce CRDS is a general procedure for measuring transient absorption and has particular advantage for rapidly evolving systems, for which the ring-down profile is nonexponential. A series of experiments have been carried out that exploits low-reflectivity mirrors with a short cavity length to demonstrate bounce-by-bounce CRDS in an empty cavity and a cavity filled with a weak absorber.

We use a linear cavity whose length may be set to a round-trip time of order 600 – 1000 fs. The mirror reflectivities are each 88 %, which is low compared to other CRDS experiments but has the advantage of delivering more power to the sample and to the detector. A pulse from a commercial mode-locked Ti:sapphire femtosecond laser of initial width 87 fs and wavelength 830 nm (with a band width of 11 nm) is introduced through the back of one of the mirrors. The femtosecond pulse train is visualized with a time microscope that utilizes the principles of parametric temporal imaging,[8, 9] which magnifies[10] the time scale by a factor of 100. Parametric temporal imaging has been described in detail elsewhere.[5–7, 9] Briefly, the time microscope expands a temporally modulated optical signal in a manner similar to how an optical microscope expands the spatial light distribution from an object. The time domain equivalent of a lens is produced by mixing, in a nonlinear optical crystal (of β-barium borate; BBO), the cavity ring-down signal with a specially prepared Gaussian pump pulse, whose phase is set to overlap the ring-down signal and whose frequency changes in time in a linear manner (linear chirped pulse). The output from the nonlinear crystal is the sum frequency of the two inputs. This up-converted output has an intensity modulation that is the product of the intensities of the two input pulses. Individual time-magnified bounces from the optical cavity are measured both in time using a streak camera (Hamamatsu) and in frequency using a spectrometer (EG&G). The finite duration of the Gaussian-shaped pump pulse limits the record length of the input to approximately 10 ps. The two measurements are calibrated temporally by making precise changes in the cavity round trip time and measuring the change in output pulse train and spectra. In principle, data can be collected with only one laser shot. In practice, the laser has a repetition rate of 80 MHz and a temporal image is averaged over 1 s to improve the signal-to-noise ratio.

Figure 1 a shows the pulse train image from an air-filled 137-μm cavity. The data do not display the familiar exponential decay profile expected in a cavity ring-down experiment owing to the use of the temporal imaging system. As in any conventional spatial imaging system, the finite aperture of the time lens causes a limited field of view; in this case about 10 ps. The effect

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is equivalent to what is called vignetting in image processing. Because the time lens pump pulse is approximately Gaussian, there is an overall Gaussian apodization to the sequence of pulses. This Gaussian profile can be accurately measured by scanning a single pulse through the entire field of view and recording the amplitude profile. Once this profile is measured, this effect can be removed from all subsequent data. Figure 1 b shows the corrected data in which the exponential decay is clearly evident. The profile is consistent with the relation given in Equation (1), where I_{in} is the initial intensity of the pulse that enters the cavity, I_n is the pulse intensity after n bounces, R is the mirror reflectivity, α is the absorption coefficient, c is the concentration, and l_s is the sample path length. The largest errors are observed at the end of the record length where the effect of the Gaussian apodization is greatest.

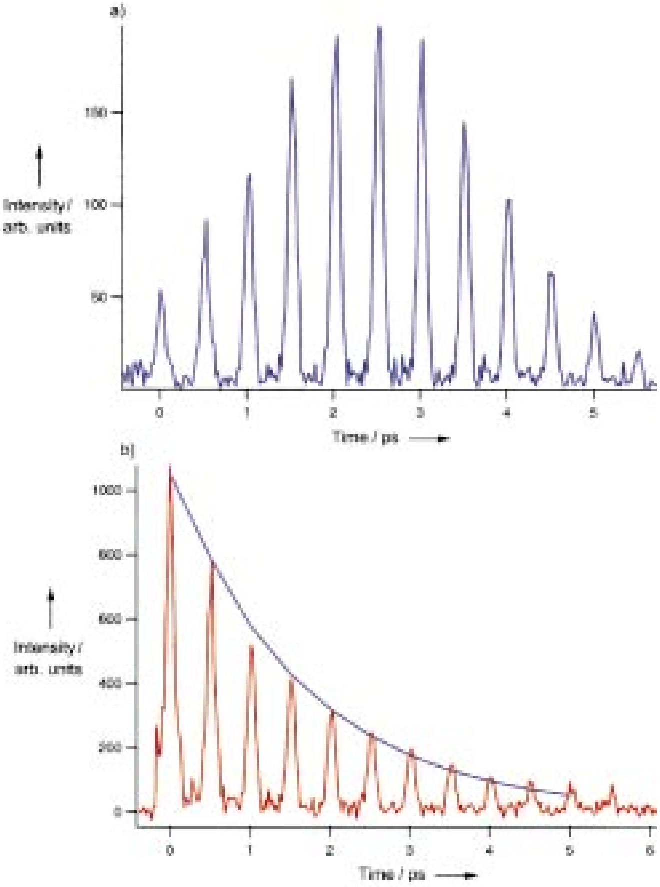

Figure 1. *Ring-down pulse profile a) apodized with a Gaussian time lens and b) with apodization removed by normalization, for an empty 137-μm optical cavity. The blue curve is the exponential fit to the data.*

$$I_n = I_{in} R^{2n} \exp[-\alpha c(n + 1/2) l_s] \qquad (1)$$

The round-trip time as measured from the spectrum is 932 ± 4 fs. The pulses have a constant separation throughout the record length, which corresponds to a cavity length of 139 ± 2 μm. This value agrees within 4% with that determined from the fringe spacings of the optical cavity. This close agreement confirms the magnification of the time microscope to be a factor of 100, within the same error. The pulses also have increased width (127 fs) compared to the output of the laser (87 fs), which is constant over the pulse train. This increase arises from dispersion of the pulse by the mirrors.

Two simple experiments demonstrate the application of bounce-by-bounce CRDS to liquid samples. Ethanol and a

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Professor Zare is renowned for his research in the area of laser chemistry, resulting in a greater understanding of chemical reactions at the molecular level. By experimental and theoretical studies he has made seminal contributions to our knowledge of molecular collision processes and contributed very significantly to solving a variety of problems in chemical analysis. His development of laser induced fluorescence as a method for studying reaction dynamics has been widely adopted in other laboratories.

Professor Zare has received numerous honors and awards, among them the ACS Nobel Laureate Signature Award for Graduate Education (2000), the E. Bright Wilson Award in Spectroscopy, the Robert A. Welch Award in Chemistry, (both 1999), the ACS Award in Analytical Chemistry (1998), the Peter Debye Award from the American Chemical Society (1991), and the Arthur L. Schawlow Award in Laser Science (2000), and the Irving Langmuir (1985) and the Earle K. Plyler (1981) Awards from the American Physical Society (APS). In May 1998, he finished serving a six-year term on the National Science Board, the last two of those years as its Chairman, for which the NSB approved a special Distinguished Service Award in his honor. In the same year, he was elected into the Royal Society of Chemistry as a Foreign Member. Most recently, it was announced that he will receive the Charles Lathrop Parson Award from the American Chemical Society in 2001.

He is currently a member of the editorial advisory boards of Angewandte Chemie, Chemical Physics Letters, ChemPhysChem, Journal of Molecular Spectroscopy, *and* Molecular Physics, *and is Chair of the Board of Directors of* Annual Reviews. *He has authored and co-authored over 625 publications.*

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solution of the laser dye IR140 (19 nM) in ethanol were introduced separately into an empty cavity with the resulting corrected pulse trains presented in Figure 2 a and b, respectively.

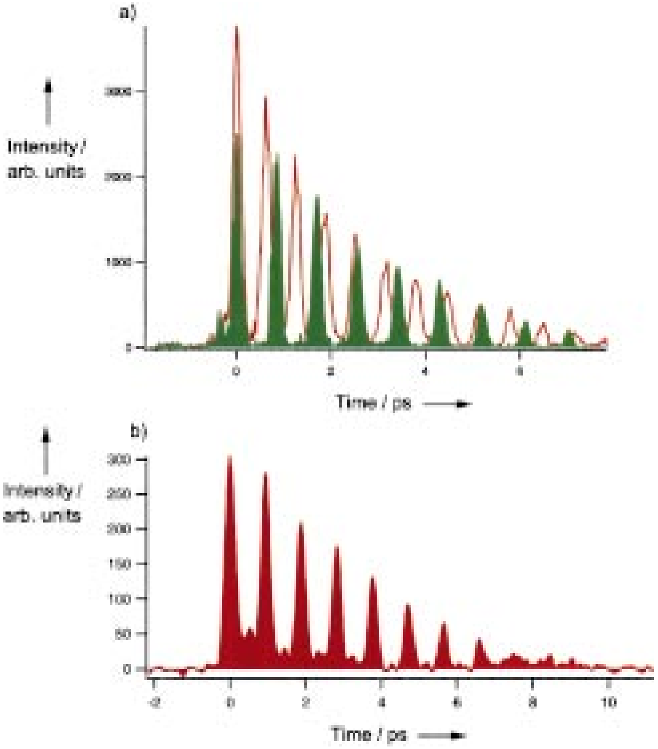

Figure 2. Ring-down pulse profile, corrected for apodization, for a 95-μm cavity; a) Empty cavity (red), ethanol (green) and b) IR140 dye dissolved in ethanol (red).

The round-trip time is significantly longer (852 ± 7 fs) in the ethanol-filled cavity than that for the empty cavity (635 ± 1 fs) owing to the refractive index of the solvent. The refractive index for ethanol may be determined by comparison of the round-trip times for the first pulse and is measured as $n = 1.345 \pm 0.012$ at 830 nm, compared with the value of $n = 1.3611$ measured at 589 nm.[11]

The cavity containing the dye solution also shows a different round-trip time corresponding to a refractive index of $n = 1.313 \pm 0.024$. The laser dye has a strong absorption at 830 nm and the change in the measured refractive index is a clear demonstration of the behavior for species that absorb at the frequency of the radiation.

Figure 3 shows the variation from bounce to bounce for the absorption of ethanol and the IR140 dye, in which we have plotted the logarithm of the intensity of a bounce, normalized to the intensity of the first bounce, as a function of the number of bounces. An exponential decrease would appear as a straight line in this plot. The data in red is for the empty cavity, that in green for ethanol, and that in blue for IR140. The ring-down profile is approximately exponential for ethanol, although it shows a slight curvature for the first few bounces. The decay for the dye solution, however, shows significant curvature and the ring-down is nonexponential. Presently, we have no complete explanation for this behavior but we believe that it may result from several factors. These factors include deviations from exponential decay caused by the saturation of the absorbing species in an intense laser field. The modeling of these results is in progress. A complete analysis must take into account absorption, stimulated emission, nonradiative processes, and reorganization of the intimate solvent shell, as well as possible coherent effects.

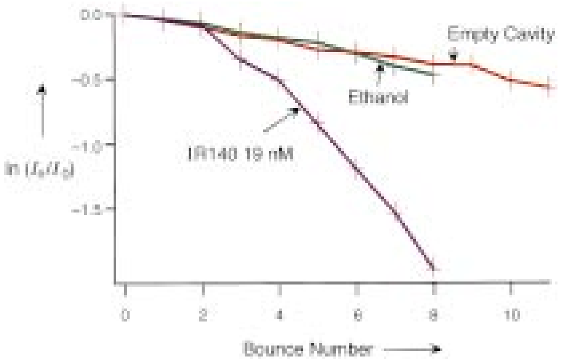

Figure 3. Logarithmic plot of the relative ring-down pulse intensity of each bounce for an optical cavity filled with: ethanol (green), IR140 dye dissolved in ethanol (blue), and comparison with the empty cavity (red).

The observations for both ethanol and IR140 illustrate some important principles that may be generalized to dynamics occurring on the time scale of the (nonexponential) ring-down pulse train. Analysis of the pulse train by visualizing each pulse shows the dynamics evolving in the sample during the time scale on the order of the round-trip time. It preserves the self-normalization advantages of cavity ring-down spectroscopy, that enables a change in the absorption to be observed that is independent of fluctuations in the light source.

The pulse train may be short so that low reflectivity mirrors or samples with significant scatter can be used as well as molecules that absorb strongly at the wavelength of interest. Low reflectivity mirrors allow more radiation to be delivered to the sample and thus open the possibility for studies of nonlinear optical processes. In addition, the low concentration (19 nM) of IR140 has been observed using the bounce-by-bounce CRDS technique and represents a significant improvement on previous liquid-phase absorption sensitivities for the same path length.

Bounce-by-bounce CRDS does not require high reflectivity mirrors, can be applied to condensed-phase samples, and may be recorded using only a single laser shot.[12] A large range of time scales is open to study by adjusting the length of the optical cavity. Temporal concentration changes on picosecond and nanosecond time scales are readily available by using cavities of millimeters to meters in length. As demonstrated in the present study, femtosecond transients can be examined, if desired, by selecting a micron-long cavity length. In the analysis of such experiments, different portions of the sample inside the optical cavity are exposed to radiation pulses from the mirror reflections at different time intervals. The time interval ranges from essentially no delay close to the mirror surfaces to the full round-trip time at the center of the cavity. Consequently, for the proper analysis of ultrafast experiments, it will be necessary to take this timing feature into account. Nevertheless, this pump-probe-probe-probe… technique does open the possibility of studying new phenomena in a manner that removes much of the uncertainty causes by light source fluctuations in more traditional, multishot pump–probe studies.

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Binding in the Ar–I$_2$(X$^1\Sigma_g^+$) Complex: A Challenge for Theory and Experiment**

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The Ar–I$_2$ van der Waals complex has been attracting attention of experimentalists and theoreticians for decades. Its ground state bond energy was deduced,[1] in terms of the measured value for the B state and shift of the I$_2$(X → B) transition, to be $D_0 = 237 \pm 3$ cm^{-1} (for the T-shaped equilibrium configuration). Recent fluorescence experiments,[2] however, suggested considerably smaller values, $D_0(L) = 172 \pm 3.5$ and $D_0(T) = 142 \pm 15$ cm^{-1} for the ground-state linear and T-shaped conformers, respectively. Both new values are smaller than 188 ± 1 cm^{-1} established[3] for the ground state (T-shaped) Ar–Cl$_2$ system, while the older value for Ar–I$_2$ is larger.

Empirical potential energy curves for corresponding diatomic species, produced by fitting data of photoionisation experiments,[4, 5] are deeper for Ar–I than for Ar–Cl, consistent with increasing dispersion interaction, which could be expected to be stronger also for Ar–I$_2$ than for Ar–Cl$_2$. Use of these empirical diatomic potentials within a diatomics-in-molecule (DIM) procedure[6] (which assumes the Ar–I interactions to be essentially unperturbed within the Ar–I$_2$ complex) leads to $D_0(T) \approx 206$ cm^{-1}. This is larger than the new experimental value but smaller than the older one by about 30 cm^{-1}, the latter difference being the same as for similar Ar–Cl$_2$ results.[7] It therefore appears that there might be a mismatch between the Ar–I and new Ar–I$_2$ experimental data interpretations.

It should be mentioned here that the note,[8] referred to also in reference [2], on the inability of the DIM method to produce the double-well topology of the ground state Ar–I$_2$ potential energy surface (PES), is valid only for the asymptotic version[9, 10] of the method. This particular approach has an inherent uncertainty in describing some molecular states, to result, in particular, in the absence of a linear conformer for the ground state. The more consistent, standard DIM procedure[6] produced two wells (for the linear and T-shaped geometries) even within the simplest diabatic, or single-state, version (see also reference [11]). This topology was confirmed later by direct ab initio calculations.[8, 12]

Ab initio results[7, 12, 13] for Ar–X$_2$ (X = Cl, Br, I) consistently approached, with increasing accuracy but still underestimated the experimental D_0 values, and predicted an increase in binding compared to the DIM results based on equivalently accurate ab initio Ar–X potentials. This means that the (effective) Ar–I interactions become more attractive within the Ar–I$_2$ complex and, hence, $D_0(T) > 206$ cm^{-1} could be expected in terms of the empirical Ar–I data, consistent with the older, but not with the new, experimental results. When such perturbations of the Ar–Cl interactions obtained from accurate ab initio calculations were transferred to the DIM results based on reliable empirical diatomic input, the measured D_0 value for Ar–Cl$_2$ was reproduced within its experimental uncertainties with no fitting.[7] Ab initio data for Ar–I and Ar–I$_2$ sufficiently accurate for similar reliable predictions are yet to be obtained.

Recent calculations[8] using a larger basis set than that employed in reference [12] within a similar ab initio method produced, expectedly, a somewhat more attractive Ar–I$_2$ interaction. Its estimated[2] bond energy was even found to match the new experimental D_0 value. However, this would mean no room for improvement exists, while a further extension of basis set could well lead to a further increase of binding. One purpose of the present work is to investigate this possibility and to try to improve further the ab initio description of the Ar–I and Ar–I$_2$ interactions. Another purpose is to bracket the true D_0 value in terms of available empirical and ab initio data and to narrow the expected interval for the Ar–I$_2$ bond energy.

Herein, empirical Ar–I potentials were used,[4] obtained from fitting data of experiments on photoelectron spectroscopy.

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