Femtosecond Relaxation Dynamics of Molecular Rydberg States Using Time-Resolved Multiphoton Ionization

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Lifetimes for $3R_g$ Rydberg states of benzene and perdeuterobenzene, and for $4d$ Rydberg states of toluene and perdeuterotoluene, have been measured by time-resolved ionization following two-photon excitation with 0.19-ps laser pulses. For benzene, this lifetime is 70 ± 20 fs. This is the shortest molecular process ever resolved by direct measurement. For toluene, the lifetime is 170 ± 20 fs. The decay mechanism is not established, but could involve internal conversion to high vibrational levels of the ground state.

Transitions to Rydberg states of phenyl molecules are difficult to observe in one-photon absorption spectroscopy because of overlap with intense, diffuse valence transitions and also because of the difficulty of working in the vacuum ultraviolet.[1] Two-photon–resonant, multiphoton ionization (MPI) spectroscopy has emerged as a valuable tool for studying these states.[2–5] Dynamical studies of phenyl Rydberg states suffer from the same difficulties as spectroscopic investigations. In some cases, lifetimes are deduced from spectral linewidths in MPI studies and suggest subpicosecond decay times.[3,4,6]

In this work, the lifetimes of Rydberg states of gas-phase benzene and toluene 64 000 cm^{-1} above the vibrationless ground state are measured directly with use of two-color MPI techniques and femtosecond dye-laser technology.[7] Lifetimes of 70 and 170 fs, respectively, are resolved. These are the shortest molecular lifetimes ever measured directly. Because of the very fast time scale, the observed decay rate corresponds to that of an ensemble under collision-free conditions. This work demonstrates the utility of time-resolved multiphoton ionization with femtosecond lasers as a sensitive technique for the study of ultrafast dynamics and reports the first results for nonradiative decay times of phenyl Rydberg states.

The experiment is illustrated schematically on an energy-level diagram for benzene in Fig. 1. A Rydberg state of benzene 63 935 cm^{-1} above the vibrationless ground state[3] is excited by two-photon absorption from a 0.19-ps pump pulse at 312.5 nm. Recent two-photon resonant MPI studies by

Whetten, Fu, and Grant[3] on jet-cooled benzene have assigned this level as the 1^1 vibronic level of a newly discovered $3R_g$ Rydberg state (0–0 transition at 62 975 cm^{-1}). The Rydberg state may be $3d$ or $4s\,^1E_{1g}$.[3] After a variable time delay, the excited state is ionized by a 0.19-ps probe pulse at 625 nm, and the resulting ion current is detected. The time evolution of the excited state is determined by the decay of ion cur-
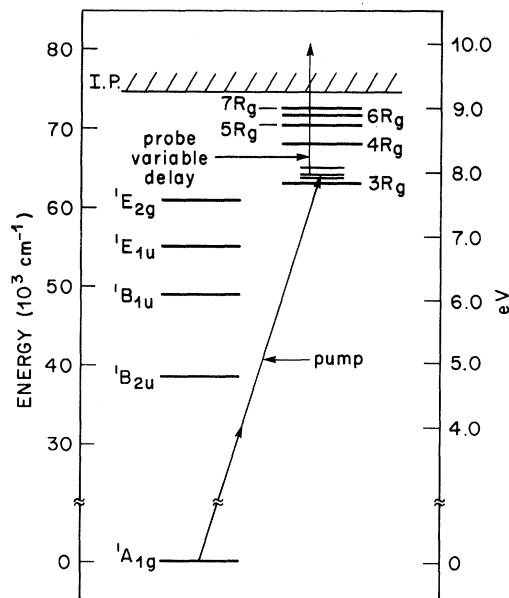

FIG. 1. Energy-level diagram of benzene (after Ref. 3) and schematic of the experiment. The $3R_g$ 1^1 level is excited by two-photon absorption. After a variable delay, molecules remaining in the $3R_g$ or $^1E_{2g}$ levels are ionized by a probe pulse at 16 000 cm^{-1}.

rent as a function of increasing time delay. There is a propensity for $\Delta v = 0$ transitions in the ionization step[6,8] so that ionization results when the probe photon energy exceeds the energy difference between the vibrationless excited state and the ionization potential. Furthermore, the ionization cross section is essentially constant above the threshold.[9] Hence, for benzene, with an ionization potential of 74 620 cm^{-1}, the probe beam will ionize all states for which the electronic origin is greater than 58 600 cm^{-1}. Thus, the present experiment will measure the sum of populations of the $3R_g$ Rydberg state and the $^1E_{2g}$ valence state.

Pulses of 0.19 ps duration (as measured by autocorrelation) at a wavelength of 625.0 nm are generated in a colliding-pulse mode-locked dye laser,[10] and amplified at a rate of 10 Hz in a neodymium-doped yttrium-aluminum-garnet–pumped, four-stage dye amplifier,[11] to produces pulses of 200 μJ energy. The pulses are divided into two beams: pump and probe. The pump beam traverses a variable optical delay and is frequency doubled in potassium dihydrogen phosphate to produce pulses of 5 μJ energy. The probe beam (50 μJ) traverses a fixed delay and passes through a quarter-wave plate and a polarizer, so that the relative polarizations of pump and probe may be varied. The two beams are recombined collinearly by a dichroic mirror and are focused by a 1.0-m lens to a spot size of 0.3 mm in the ion-collection region of the evacuable sample cell. The ion-collection region consists of two straight tungsten wire electrodes separated by 1.5 cm. The ion currents are detected by a picoammeter in series with the electrodes and a 200-V battery. The variable time delay is controlled by a microcomputer which also digitizes and stores the ion current signal.

Benzene, toluene, and their fully deuterated analogs were spectral grade and NMR spectral grade reagents, respectively. The samples were degassed in the sample cell by repetitive freeze-pump-thaw cycles. Experiments were performed at ambient pressures above the liquid at 22 C (80 Torr for benzene and 30 Torr for toluene).[12] At 80 Torr, the mean time between gas-kinetic collisions is 1 ns, so that the results reported here certainly are in the collision-free regime.

The time-resolved ion current for excitation of the $3R_g$ 1_0^1 transition of benzene is shown in Fig. 2. The signal level scales quadratically for the 312.5-nm pump beam over a fivefold variation of intensity, and linearly for the 625-nm probe
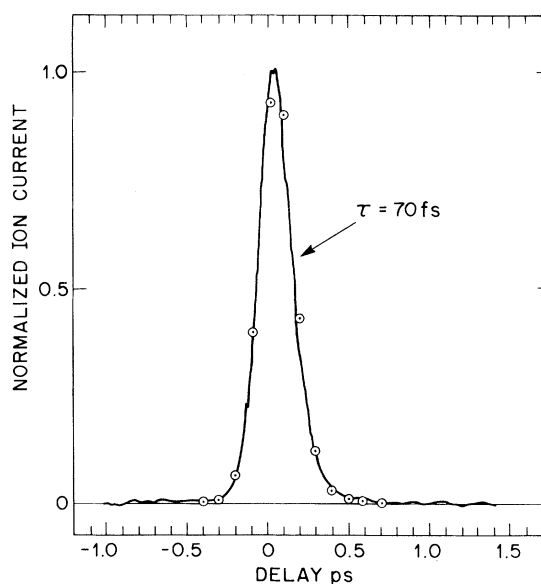

FIG. 2. Lifetime of the $3R_g$ Rydberg state of benzene. The solid line is the time-resolved ion current. The circles are results of a model calculation assuming a pulse width of 190 fs, and a decay time of 70 fs. The baseline has been adjusted to remove a small (less than 10%) time-independent ionization signal.

beam over a fourfold intensity variation. The temporal behavior of the signal is identical when the probe beam is attenuated by a factor of 4, indicating that the rate of ionization due to the probe beam does not compete with the unimolecular decay rate of the Rydberg state.[2] The signal level and temporal behavior are unaffected by relative polarization of pump and probe beams.

The lifetime is extracted by numerical modeling of the data, with the assumption of visible and uv pulses of Gaussian shape and 0.19 ps full width at half maximum (points in Fig. 2). The rise of the ion current is sharper than that of the measured pulse autocorrelation, since excitation is due to two photons, so that the rise follows the integral of the square of the excitation pulse intensity. A decay time of 70 ± 20 fs is deduced from the modeling. This is the fastest decay rate ever measured directly.

The measured lifetime is in good agreement with that deduced from the two-photon linewidth of the $3R_g$ 1_0^1 transition, measured to be 59 cm^{-1} (90 fs).[3] This agreement suggests that the $^1E_{2g}$ valence state is not a bottleneck in the decay of the $3R_g$ Rydberg state, because the $^1E_{2g}$ state, as discussed above, could be ionized by the probe pulse. The experiment was repeated with perdeuterobenzene excited to the same Rydberg state

($3R_g$ 1_0^1 transition at 63 935 cm^{-1}).[3] The measured lifetime is 110 ± 20 fs, slightly larger than for benzene.

The lifetimes of the $3R_g$ Rydberg state in benzene and perdeuterobenzene are very short, even though Rydberg states are not as strongly coupled to the molecular core as valence states. The propensity of MPI spectroscopy, with nanosecond lasers, to observe Rydberg states is due to their long lifetime relative to valence states.[2,4] Therefore, the lifetimes of the higher valence states of benzene must be extremely short.

What is the decay mechanism for the $3R_g$ Rydberg state? Consider first the higher valence states. Excitation into the $^1B_{1u}$ or $^1E_{1u}$ states of benzene vapor is not followed either by internal conversion to $^1B_{2u}$ or by intersystem crossing.[13] Ultimately, photochemical products are possible, and they may be formed after the valence states have decayed rapidly by internal converstion to very high vibrational levels of the ground state.[14,15] Indeed, very rapid internal conversion to high vibtational levels of the ground state appears to occur and be responsible for "channel three" relaxation in the $^1B_{2u}$ state.[16] The valence isomers of benzene may be involved as products of the very highly excited ground state[14,15] or as intermediates in the relaxation of the higher valence states.[17] The $3R_g$ Rydberg state may decay by a mechanism similar to those for the $^1B_{1u}$ or $^1E_{1u}$ states. Internal conversion from the $3R_g$ state is due to rotation-vibration-electron coupling between the Rydberg electron and the cationic core. Such a process may be viewed within the framework of multichannel quantum-defect theory.[18-20] Internal conversion from $3R_g$ might proceed via a cascade process through lower Rydberg states. A time-resolved MPI study with a higher-energy probe pulse would be useful in elucidating the mechanism. At any rate, since the decay times for proto and deutero forms of benzene are not very different, the rate-determining step does not involve excitation of C-H stretching modes.

The spectroscopy of toluene is not as well studied as that of benzene. The valence states of toluene have their analogs in those of benzene, and the one-photon spectra are similar.[1,21,22] Energies of the lowest three excited valence states are 37 500 cm^{-1} ($^1B_2$ state), 46 500 cm^{-1}, and 53 000 cm^{-1} (Ref. 22). In recent work, Grant and co-workers[23] have identified a $4d$ 0_0^0 two-photon transition in toluene at $64 060 \pm 10$ cm^{-1}. This is the Rydberg state excited in the present experiment.
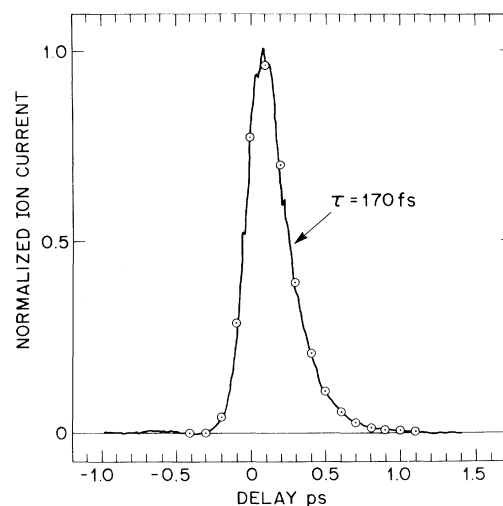

FIG. 3. Lifetime of the $4d$ Rydberg state of toluene. The solid line is the time-resolved ion current, and the points are the result of a model calculation, yielding a decay time of 170 fs. The baseline has been adjusted as in Fig. 2.

The time-resolved behavior of the $4d$ Rydberg state of toluene is shown in Fig. 3. The lifetime of 170 ± 20 fs is derived by the modeling procedure described previously. The spectroscopic linewidth for the $4d$ 0_0^0 transition is 38 cm^{-1} (140 fs),[23] in good agreement with the time-resolved data. For perdeuterotoluene, the lifetime of the $4d$ state is 190 ± 20 fs. The mechanism of this extremely rapid decay is unclear, but it may also involve highly vibrationally excited levels of the ground electronic state. As with benzene, no emission is observed from the $^1B_2$ state after exciting into the second and third valence states of toluene vapor.[13] Because of the similarity of lifetimes of prototoluene and deuterotoluene, the decay of the $4d$ Rydberg state does not involve C-H stretching modes.

In summary, the time scale for decay of Rydberg states of benzene and toluene, ~100 fs, has been established by direct measurement. Further experiments, perhaps using a shorter-wavelength probing beam, will help elucidate the mechanism for the decay of these states. With use of femtosecond dye-laser technology and multiphoton ionization techniques, a method now exists to study the dynamics of molecules with very high levels of electronic excitation. New and exciting results should be forthcoming.

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