Coherent laser control of the resonance-enhanced multiphoton ionization of HCl

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A long-standing goal of photochemistry is the use of radiation to control the distribution of products in chemical reactions. The properties of laser radiation, including monochromaticity, high intensity, short pulse duration, and phase coherence, offer many new strategies for achieving this goal. With some notable exceptions,[1,2] most attempts at bond-selective photochemistry using a single laser beam have been disappointing. The reason for this failure is that in a multichannel reaction the states excited by a single photon are usually superpositions spanning more than one set of possible products, and variation of the wavelength or intensity of the laser provides little control over the branching between different reaction channels.

To overcome this fundamental difficulty, various theoretical schemes utilizing more than one laser have been developed. One of these methods, pioneered by Tannor and Rice,[3] uses two ultrashort pulses in a pump-and-probe arrangement. With this method an intense pump laser pulse prepares a wave packet on an electronically excited surface, and after a chosen interval a second laser pulse dumps the evolving wave packet into a selected region of the ground potential energy surface. Optimum control theory,[4] first applied by Rabitz and co-workers[5] to this problem, can be used to tailor the temporal profile of the electric field to maximize control of the reaction.

A different approach first proposed by Brumer and Shapiro[6] uses two weak laser pulses to excite the molecule simultaneously by two distinct optical paths. The key property of these pulses is that they have a coherent and adjustable phase difference. The pulses populate a coherent, degenerate state which correlates to a linear combination of the possible reaction products. By adjusting the relative phases of the two beams it is possible to alter this combination in such a way as to enhance one product channel at the expense of the other.

There are a variety of ways of selecting the two optical paths. The method we have chosen, which was first proposed by Shapiro, Hepburn, and Brumer[7] (SHP), consists of excitation by three photons of frequency ω_1 along the first path, and excitation by one photon of frequency $\omega_3 = 3\omega_1$ along the second path. In a detailed calculation Chan *et al.*[8] demonstrated that this method can achieve a considerable degree of control in the photodissociation of IBr. Recently Elliott and co-workers[9] employed a similar excitation scheme in the resonance-enhanced multiphoton ionization (REMPI) of Hg atoms in a bulb. In the present study we have used the SHP method to ionize different rotational states of a diatomic molecule in a pulsed molecular beam.

The apparatus will be described in detail in a future publication. Briefly, 336 nm radiation (ω_1 in the SHP scheme) was generated by frequency doubling the output of a tunable dye laser, which used a mixture of DCM and LDS 698 dyes. An injection-seeded Nd:YAG laser (Continuum YG681C) was used to pump a narrow bandwidth (0.03 cm^{-1}) dye oscillator (Pegasus) to generate the 672 nm fundamental. This laser operates on only three longitudinal modes, with most of the energy carried by the center mode. Three or four home-made longitudinal amplifier stages were used to amplify the fundamental while maintaining good beam quality. The UV radiation had a typical pulse energy of 1.5 mJ and a duration of 5 ns. The relative energy of the UV beam was monitored continuously with a photodiode.

VUV radiation (ω_3) was obtained by focusing the UV beam with a 100 mm quartz lens into a cell containing Kr gas, which was used as a third harmonic generation medium.[10] Using a design similar to that of Chen and Elliott,[9(a)] the ω_1 and ω_3 beams were focused into the apparatus by a pair of VUV mirrors (Acton, No. 1200 with broadband Al + MgF_2 coating) with an incidence angle of $\approx 4°$. The phase difference of the two beams was varied by passing both beams through a gas having strong dispersion near ω_3. The phase difference for three photons of frequency ω_1 and one photon of ω_3 is given by

$$\Delta\theta = 3\theta_1 - \theta_3 = l\omega_3(n_3 - n_1)/c, \tag{1}$$

where l is the path length, n_i is the index of refraction at frequency ω_i, and c is the speed of light. The difference $n_3 - n_1$ is proportional to the pressure of the tuning gas. Phase tuning in our experiment was accomplished by filling the chamber containing the two focusing mirrors with either Ar or H_2, with a path length of $l = 46$ cm. The pressure of the tuning gas was measured with a capacitance manometer (Datametrics 600, 10 Torr head).

Ionization of HCl was accomplished in a newly constructed molecular beam machine equipped with a home-made time-of-flight mass spectrometer. Neat HCl (Matheson, 99.0%) was expanded into the main vacuum chamber by a pulsed nozzle (Newport BV-100) with a stagnation pressure of ≈ 300 Torr. A set of Wiley–McLaren[9] electrodes and Einsel lenses was used to accelerate and focus the ion beam onto a multichannel plate detector (Jordan Co.). The molecular beam and the focal point of the two laser beams intersected between the repeller and extractor electrodes. The ground electrode consisted of a polished plate with a 2 mm diam aperture. The focal point of the

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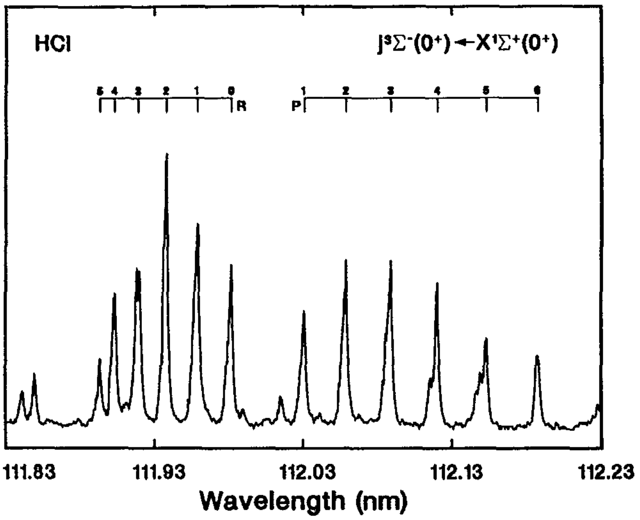

FIG. 1. REMPI spectrum of the $j\,^3\Sigma^-(\Omega=0^+,\ v'=0) \leftarrow X(^1\Sigma^+, v''=0)$ transition showing P and R branches. Ionization is produced by both 1 + 1 and 3 + 1 excitation.

laser beams was adjusted to lie under this hole so that only ions produced by both the ω_1 and ω_3 beams were detected. The signals from the ion detector, photodiode, and capacitance manometer were sent to a three channel boxcar averager (Stanford SR250), which was interfaced to a laboratory computer.

In order to achieve population control by varying $\Delta\theta$ it is necessary that both the 1 + 1 and 3 + 1 REMPI processes,

$$\mathrm{HCl}(v''=0, J'') + \omega_3 \rightarrow \mathrm{HCl}^*(v', J') \tag{2a}$$

and

$$\mathrm{HCl}(v''=0, J'') + 3\omega_1 \rightarrow \mathrm{HCl}^*(v', J') \tag{2b}$$

followed by

$$\mathrm{HCl}^* + \omega_1 \rightarrow \mathrm{HCl}^+, \tag{3}$$

have comparable rates. We found empirically that this condition could be satisfied by using the $j^3\Sigma^-(0^+)$ state of HCl as the resonant intermediate state. The REMPI spectrum for the P and R branches of the 0–0 transition with both the ω_1 and ω_3 beams on is shown in Fig. 1. The rotational constant calculated from this spectrum (9.60 cm^{-1}) is in excellent agreement with the previously reported values.[12]

Coherent phase control of the ionization rate was obtained for all of the lines assigned in Fig. 1. For each transition, the Kr pressure in the tripling cell was adjusted so that the 1 + 1 and 3 + 1 MPI rates were nearly equal. The tuning gas pressure was then continuously scanned. The results for the $R(2)$ transition are shown in Fig. 2, displaying a modulation depth of ≈40%. With Ar as a tuning gas a phase change of 2π is produced by a pressure change ΔP of 0.43 ± 0.01 Torr. This value corresponds to an index of refraction difference of $\Delta n = (4.7 \pm 0.1)\times10^{-4}$ (at 1 atm. and 273 K), which is in excellent agreement with the experimental[13] value of 4.5×10^{-4} and the calculated[14] value of 4.6×10^{-4}. Using H_2 as a tuning gas we obtain $\Delta P = 0.51\pm0.02$ Torr, which corresponds to $\Delta n = (4.0\pm0.2)\times10^{-4}$ and $n-1 = (5.4\pm0.2)\times10^{-4}$ at 1119.4 Å. To our knowledge there are no other experimental or theoretical values of n available for H_2 at this wavelength.

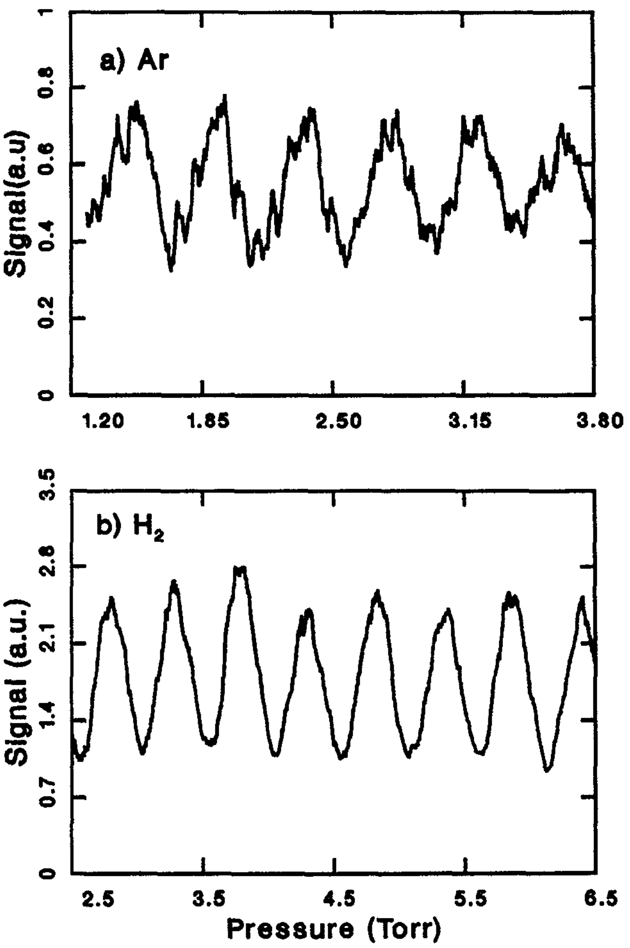

FIG. 2. Ionization signal for the $R(2)$ transition as a function of pressure in the tuning cell, using either (a) Ar or (b) H_2 to control the relative phases of ω_1 and ω_3.

The sinusoidal variation of the product yield illustrated in Fig. 2 was predicted by SHP. The wave function of the resonantly excited state, $\Psi(t)$, is given by a sum of one- and three-photon excitation terms,

$$\begin{aligned}\Psi(t) = \sum_{M'} & |J',M'\rangle \exp(-iEt/\hbar) \\ & \times \langle J',M'|\{\epsilon_3 \exp[i(\theta_3 + \mathbf{k}_3\cdot\mathbf{z})]\,\hat{\epsilon}_3\cdot\boldsymbol{\mu} - \epsilon_1^3 \\ & \times \exp[3i(\theta_1 + \mathbf{k}_1\cdot\mathbf{z})]\}\mathbf{T}|J'',M''\rangle.\end{aligned} \tag{4}$$

In Eq. (4) E is the term value of the resonant intermediate state, ϵ_i are the one- and three-dimensional electric field intensities (with unit vectors $\hat{\epsilon}_i$), $\mathbf{k}_i$ are the corresponding wave vectors, $\boldsymbol{\mu}$ is the transition dipole operator, $\mathbf{T}$ is the three-photon transition operator,[15] and the summation is over magnetic quantum numbers. The ionization rate Γ is proportional to the population of the resonantly excited state; i.e.,

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$$\Gamma \propto \epsilon_3^2 \sum_{M',M''} |\langle J',M'|\,\hat{\epsilon}_3\cdot\boldsymbol{\mu}\,|J'',M''\rangle|^2 + \epsilon_1^6 \sum_{M',M''} |\langle J',M'|\mathrm{T}|J'',M''\rangle^2 - 2\epsilon_3\,\epsilon_1^3 \times\cos(\Delta\theta+\delta_{13})\,|F_{13}|, \tag{5}$$

where $F_{13}\exp(i\delta_{13})$ is the cross term matrix element. The modulation depth is determined by the relative magnitudes of F_{13} and the one- and three-photon transition probabilities, which are given by the first two terms of Eq. (5).

It is important to consider the possible spatial variation of the phase difference between the two beams. One possible effect is a rapid spatial fluctuation caused by the $3\mathbf{k}_1\cdot\mathbf{z}-\mathbf{k}_3\cdot\mathbf{z}$ term, which results from squaring Eq. (4). For plane waves the phase matching condition $\mathbf{k}_3 = 3\mathbf{k}_1$ assures that this term vanishes. In addition there remains a slow phase variation in the vicinity of the focal point of the two Gaussian beams.[9(b)] In our apparatus this effect is negligible because of the small field of view of the 2 mm aperture in the ion optics.

Interference effects in the MPI of atoms and molecules are well known.[16] In particular, many studies have demonstrated that third harmonic generation can suppress[17–22] (and in some cases enhance[23,24]) MPI, both coherently and incoherently.[25] In these earlier studies ω_3 was generated within the excited medium, and alteration of the ionization rate was achieved by varying the gas pressure. While these effects are closely related to the one reported here, they do not readily lend themselves to active control of photochemical reactions. In the present work and in the study of Chen *et al.*,[9] ω_3 is supplied externally and the reaction rate is controlled actively in a predictable and noninvasive fashion by varying the relative phases of the two beams. The population control demonstrated here for a single channel molecular process is a crucial step for controlling branching ratios in multichannel reactions.

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