

Polarization Control of Branching Ratios in Photodissociation

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It is shown that product ratios in photodissociation differential cross sections can be controlled experimentally by variation of the polarization of the exciting laser. For M -selected initial states, where M is the angular momentum projection quantum number of the initial bound level, control can be complete insofar as one can totally eliminate production of a selected product-arrangement channel. Further we show that control survives M averaging for ${}^1\Sigma \rightarrow {}^1\Pi$ systems. The method is applied to model diatomic ${}^1\Sigma \rightarrow {}^1\Sigma$ and ${}^1\Sigma \rightarrow {}^1\Pi$ photodissociation.

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The use of lasers to control product populations in dissociation and scattering has long been a goal in molecular physics.¹ Recent theoretical work² has shown that the essence of controlling photodissociation products lies in the ability to alter directly, through coherent excitation, the amplitudes and phases of components of stationary energy eigenstates in the continuum. At present, experimental verification of this fundamental approach to laser-controlled reaction dynamics is hampered by the need for multiple, phase-matched, excitation frequencies with well-defined relative phases.

In this paper, we eliminate these restrictions by demonstrating that active control over differential cross sections can be obtained with a single laser frequency of variable elliptic polarization. A wide range of yield control is shown to be attainable for an M -selected state, where M is the angular-momentum projection quantum number for the initial bound level. In many systems a substantial degree of control also survives averaging over M . As a consequence of this result, experimental verification of the principle of coherent control is within immediate experimental reach. Below, we restrict attention to diatomic photodissociation although qualitative features are the same for polyatomic systems.

Standard treatments of photodissociation³ give the rate of radiant energy absorption per unit angle, associated with the transition from an initial bound state $|\psi_0\rangle$ into arrangement channel q , as

$$dR_q/d\Omega_k = E_p |T_q(M, \theta_k, \phi_k)|^2. \quad (1)$$

Here E_p is the photon energy, and $T_q(M, \theta_k, \phi_k) = \langle \psi_0 | \boldsymbol{\epsilon} \cdot \mathbf{d} | \psi_q^- \rangle$, where \mathbf{d} is the dipole moment and $\boldsymbol{\epsilon}$ is the polarization vector. The state $|\psi_0\rangle$ is defined by energy E_0 , and vibrational, rotational, and rotational-projection quantum numbers v_0 , J_0 , and M . The continuum ket $|\psi_q^- \rangle$, also an exact eigenstate of the total

molecular Hamiltonian, describes a final state with momentum \mathbf{k}_q that dissociates into channel q and obeys incoming boundary conditions. The angles $\Omega_k = (\theta_k, \phi_k)$ define the space-fixed orientation of \mathbf{k}_q . For brevity, the dependence of $T_q(M, \theta_k, \phi_k)$ on θ_k and ϕ_k will henceforth be suppressed, as are the J_0 , v_0 , and E_0 dependences. Note that we assume a system in which \mathbf{k}_q specifies the asymptotic state completely. Remarks on systems with additional degeneracies are provided later below.

In general, the polarization vector is given by

$$\boldsymbol{\epsilon} = \epsilon_1 e^{i\alpha_1} \hat{\boldsymbol{\epsilon}}_1 + \epsilon_2 e^{i\alpha_2} \hat{\boldsymbol{\epsilon}}_2, \quad (2)$$

where $\hat{\boldsymbol{\epsilon}}_s$ ($s=1,2$) are orthonormal vectors, and ϵ_s, α_s are real. We choose space-fixed coordinates such that the z axis coincides with $\hat{\boldsymbol{\epsilon}}_1$ and the negative y axis with $\hat{\boldsymbol{\epsilon}}_2$ so that $\Omega_s = (\theta_s, -\pi/2)$ is the space-fixed orientation of $\hat{\boldsymbol{\epsilon}}_s$.

The probability of our obtaining products in channel q at the indicated angles is

$$P^{(q)}(M, \theta_k, \phi_k) = \frac{|T_q(M)|^2}{\sum_n |T_n(M)|^2},$$

where n runs all over the product channels; the branching ratio $R_{qq'}$ is given by $|T_q(M)|^2/|T_{q'}(M)|^2$. With the definitions $T_{qs} = \langle \psi_0 | \hat{\boldsymbol{\epsilon}}_s \cdot \mathbf{d} | \psi_q^- \rangle$ and $I_{ss'}^{(q)} = T_{qs}^* T_{q's}$, the ratio can be written as

$$R_{qq'} = \frac{\epsilon_1^2 I_{11}^{(q)} + \epsilon_2^2 I_{22}^{(q)} + 2\epsilon_1 \epsilon_2 \cos(\alpha_2 - \alpha_1 + \alpha_{12}^{(q)}) |I_{12}^{(q)}|}{\epsilon_1^2 I_{11}^{(q')} + \epsilon_2^2 I_{22}^{(q')} + 2\epsilon_1 \epsilon_2 \cos(\alpha_2 - \alpha_1 + \alpha_{12}^{(q')}) |I_{12}^{(q')}|}. \quad (3)$$

The integrals $I_{ii}^{(q)}$ ($i=1,2$) are real, whereas $I_{12}^{(q)}$ is complex with phase $\alpha_{12}^{(q)}$. Note that all $I_{ij}^{(q)}$, as well as $R_{qq'}$, depend on the scattering angles θ_k and ϕ_k .

Experimental control over $R_{qq'}$ is therefore obtained by the variation of the phase difference $\alpha_2 - \alpha_1$ and of the amplitude parameter $S = \epsilon_2^2/(\epsilon_1^2 + \epsilon_2^2)$, i.e., the degree

of elliptical polarization of the incident light. Since the $I_{12}^{(q)}$ and $I_{12}^{(q)}$ terms affect R_{qq} , the resultant ratio is not just the sum of linear polarization contributions. That is, the cross term introduces interference effects through the phase difference $\alpha_2 - \alpha_1$. Note, in this regard, that the spatial phase of the electric field cancels out of all relevant expressions.

The extent of achievable control in this case is considerable. Note that by definition, $|I_{12}^{(q)}|^2 = I_{11}^{(q)} I_{22}^{(q)}$. Hence, if experimental parameters are tuned such that $S = I_{11}^{(q)} / (I_{11}^{(q)} + I_{22}^{(q)})$, and $\alpha_2 - \alpha_1 = \pi - \alpha_{12}^{(q)}$, then $|T_q(M)|^2 = 0$, i.e., *any selected q channel may be completely suppressed in the photodissociation!* Thus, for a system with two exit arrangement channels specified by \mathbf{k}_q , R_{qq} may be tuned to either 0 or infinity, i.e., variation of the polarization of a laser incident on an M -specific state gives 0–100% control over the product yield at a fixed detection angle.

The branching ratio R_{qq} has the same form as the ratio derived in Ref. 2 for the integrated cross section for photodissociation from an initial superposition of two bound states that dissociates under the influence of two lasers. Control there derives from parameters that characterize the relative intensities and phases of two lasers, whereas control here derives from parameters that characterize the polarization of one laser. In both cases the variation of the experimental parameters directly alters the constitution of the created superposition state,

$$F_{nq}^- = \frac{1}{4\pi} \sum_{J=0}^{\infty} \sum_{M=-J}^J i^J (2J+1) D_{M\Lambda}^{J*}(\phi_k, \theta_k, 0) D_{M\Lambda}^J(\phi, \theta, 0) \psi_{nq}^{J-}(R)/R, \quad (7)$$

where Λ is the absolute value of the z component of the electronic angular momentum; $\Lambda = 0$ for Σ states and $\Lambda = 1$ for a Π state.

Experimentally, it is easier to work with non- M -selected initial states, and so we consider the M average $\langle |T_q|^2 \rangle = (2J_0 + 1)^{-1} \sum_M |T_q(M)|^2$ and associated probability $\langle P^{(q)} \rangle$. The M sum is performed with use of Eq. 4.6.2 in Ref. 5, with the result

$$\langle |T_q|^2 \rangle = \frac{e^2 \sigma_q^{(\Lambda)}}{12\pi(1+\Lambda)} \epsilon^2 [1 + \beta_q^{(\Lambda)} B(\theta_k, \phi_k) + \rho_q^{(\Lambda)} R(\theta_k, \phi_k)], \quad (8)$$

with

$$B(\theta_k, \phi_k) = \epsilon^{-2} [\epsilon_1^2 P_2(\cos\theta_k) + \epsilon_2^2 P_2(-\sin\theta_k \sin\phi_k) + 3\epsilon_1 \epsilon_2 \cos(\alpha_2 - \alpha_1) \cos\theta_k \sin\theta_k \sin\phi_k],$$

and

$$R(\theta_k, \phi_k) = 3 \frac{\epsilon_1 \epsilon_2}{\epsilon^2} \cos(\alpha_2 - \alpha_1) \sin\theta_k \cos\phi_k,$$

where P_2 is the second-order Legendre polynomial and $\epsilon^2 = \epsilon_1^2 + \epsilon_2^2$. Here the coefficient $\sigma_q^{(\Lambda)}$ is the integrated cross section, $\beta_q^{(\Lambda)}$ is the anisotropy factor, and $\rho_q^{(\Lambda)}$ is a factor due to the interference of the two laser components.⁶

For an M -averaged case, extensive control is no longer guaranteed and determination of the yield range requires examination of $\langle |T_q|^2 \rangle$. It is easy to show that for ${}^1\Sigma \rightarrow {}^1\Sigma$ this range does not exceed that attainable by

reflecting the essential principle of coherent control.

To compute R_{qq} , as well as to consider the case of non- M -selected initial states, requires specification of the symmetries of the states. Here, we discuss diatomic ${}^1\Sigma \rightarrow {}^1\Sigma$ and ${}^1\Sigma \rightarrow {}^1\Pi$ transitions and describe the initial bound state by the Born-Oppenheimer function $\psi_0 = F_0(\mathbf{R})\phi_0(\mathbf{r}; R)$, where \mathbf{R} is the space-fixed separation between the fragments and \mathbf{r} denotes the electronic coordinates of the system. The coupled-channels wave function is taken as

$$\psi_q^-(\mathbf{R}, \mathbf{r}; \mathbf{k}) = \sum_{n=1}^N F_{nq}^-(\mathbf{R})\phi_n(\mathbf{r}; R), \quad (4)$$

where N is the number of channels available to the system. In terms of nuclear functions, T_{qs} is then⁴

$$T_{qs} = -e \left(\frac{4}{3}\pi\right)^{1/2} \sum_{p\nu} Y_{1p}^*(\Omega_s) \langle F_{nq}^- | D_{p\nu}^{1*} \mu_{n0}^{(q)} | F_0 \rangle, \quad (5)$$

where p runs from -1 to 1 , D is the rotation matrix,⁵ and e is the electron charge. The dipole intensity $\mu_{n0}^{(q)}(R)$ is given by

$$\mu_{n0}^{(q)} = \sum_j \left(\frac{4}{3}\pi\right)^{1/2} \langle \phi_n | r_j Y_{1j}(\Omega_j) | \phi_0 \rangle, \quad (6)$$

where (r_j, Ω_j) are body-fixed coordinates of the j th electron. Below, $\Omega = (\theta, \phi)$ denotes the orientation of \mathbf{R} .

The nuclear ground state can be written as $F_0 = Y_{J_0 M}(\Omega) \psi_{v_0}^{J_0}(R)/R$ and the nuclear portion of the final-state function expanded in partial waves:

variation of the angle of detection after excitation with a linear polarization. To see this note that $\rho_q^{(0)} = 0$ so that for a ${}^1\Sigma \rightarrow {}^1\Sigma$ transition the third term drops out of Eq. (8). With the definitions $b = \epsilon_1 |\cos\theta_k|$, $c = \epsilon_2 |\sin\theta_k \sin\phi_k|$, and

$$A = \alpha_2 - \alpha_1 - \pi H(\cos\theta_k \sin\theta_k \sin\phi_k),$$

where $H(x) = 0$ for $x < 0$ and unity otherwise, then $a^2 = b^2 + c^2 - 2bc \cos A$, and $B(\theta_k, \phi_k) = (3a^2 - \epsilon^2)/2\epsilon^2$. In this form it is clear that the minimum of $\beta(\theta_k, \phi_k)$ (and hence $\langle |T_q|^2 \rangle$) occurs at $A = 0$, $a = 0$, and the maximum at $A = \pi$, both of which are linear polarization

cases. The polynomial $B(\theta_k, \phi_k)$ varies between $-\frac{1}{2}$ and 1, which is the same as the range of the Legendre polynomial that appears in the linear polarization result. Thus, for a ${}^1\Sigma \rightarrow {}^1\Sigma$ transition where M is not selected, there is no advantage to controlling yield via the laser polarization. However, in general, $\rho_q^{(1)} \neq 0$, and so control beyond the range accessible with linear polarization is still expected in the ${}^1\Sigma \rightarrow {}^1\Pi$ case.

To demonstrate the results of polarization control, we consider a two-state model constructed by substantial modification of LiF potentials.⁷ Consider first a ${}^1\Sigma \rightarrow {}^1\Sigma$ case with ground state described by the potential

$$V(R) = R^{-4} + 0.302 \{ e^{-1.2(R-2.92)} - 2e^{-0.6(R-2.92)} \}.$$

This potential also describes the second excited state and has an asymptotic energy of 0.07503 a.u. Excited state 1, which crosses $V(R)$ at $R=6.3a_0$, is taken as the repulsive covalent ${}^1\Sigma$ diabatic potential of LiF (Ref. 7); its asymptote defines the zero of energy. These excited-state potentials are then coupled through diabatic coupling terms equal to one-half that of LiF (Ref. 4). The Franck-Condon approximation is assumed, with $\mu_{10} = \mu_{20} = 10$.

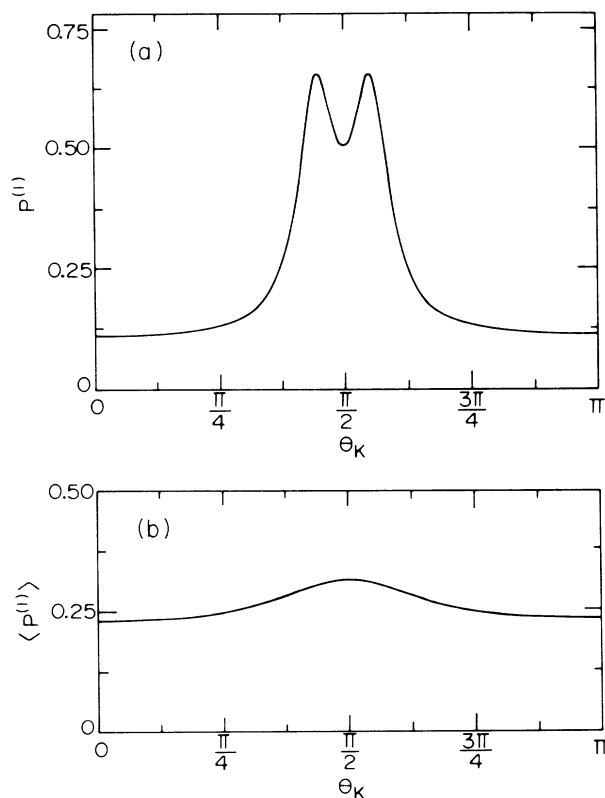


FIG. 1. Probability $P^{(1)}$ of dissociation into channel 1 in photodissociation with a laser linearly polarized along the z axis. (a) ${}^1\Sigma \rightarrow {}^1\Sigma$, $(v_0, J_0, M) = (0, 1, 0)$; (b) ${}^1\Sigma \rightarrow {}^1\Pi$, $(v_0, J_0, M) = (0, 1)$ and averaged over M .

Consider first photodissociation via a linearly polarized laser along the z axis; $P^{(1)}$ is shown in Fig. 1(a) for an M -selected initial state. The probability is seen to vary between 0.11 and 0.65. Similarly, for linear polarization along any axis the probability was found to vary between 0.05 and 0.65. By contrast, results for variable elliptical polarization are shown in Fig. 2 which shows $P^{(1)}$ contours as a function of S and $\alpha_2 - \alpha_1$ at a specific detection angle. The probability is seen to span the full range, reaching zero and unity at the indicated experimental S and $\alpha_2 - \alpha_1$ values. We thus numerically confirm that one obtains 0–100% control in a system that gives only a limited range of yields in photodissociation via linear polarization. As noted above, this effect vanishes upon M averaging, for the ${}^1\Sigma \rightarrow {}^1\Sigma$ case. In contrast, consider a second case where the excited states described above are assigned ${}^1\Pi$ symmetry and the ground state is taken as the ${}^1\Sigma$ ionic LiF potential. Our principle interest in this case is in displaying control in the M -averaged initial state. Consider then Fig. 3 which shows $\langle P^{(1)} \rangle$ vs S at different values of $\alpha_2 - \alpha_1$; the probability is seen to vary between 0.2 and 0.7. Figure 1(b) shows, for comparison, the results for linear polarization in which $\langle P^{(1)} \rangle$ is seen to be limited to 0.23–0.34. The utilization of variable elliptical polarization thus results in an enormous increase in the probability of producing product 1 at fixed angle.

We have shown that optimum polarization control over yield at fixed angle results for M -selected initial states in systems where \mathbf{k}_q defines the asymptotic state. This control is expected to be somewhat degraded in systems with additional degeneracies⁸ (e.g., additional elec-

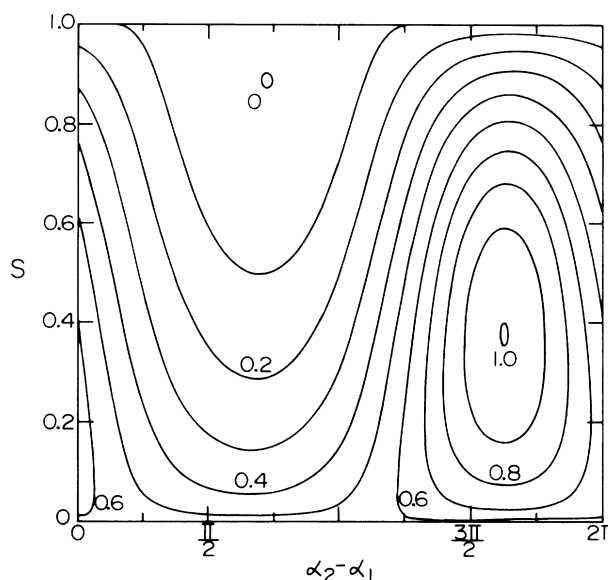


FIG. 2. Contours of constant $P^{(1)}$ in ${}^1\Sigma \rightarrow {}^1\Sigma$ photodissociation as a function of amplitude ratio S and phase difference $\alpha_2 - \alpha_1$. Results are at $(\theta_k, \phi_k) = (85^\circ, 30^\circ)$ for $(v_0, J_0, M) = (0, 1, 0)$.

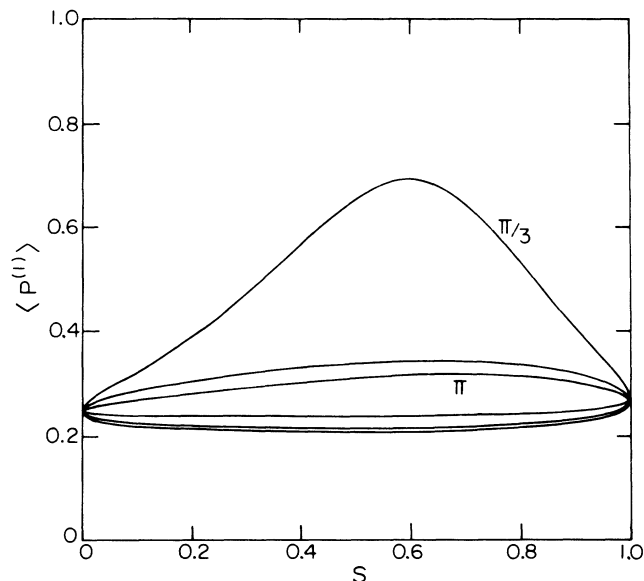


FIG. 3. Probability $\langle P^{(1)} \rangle$ in ${}^1\Sigma \rightarrow {}^1\Pi$ photodissociation from M -averaged initial state with $(v_0, J_0) = (0, 1)$. Curves are for fixed $\alpha_2 - \alpha_1$ with top curve at $\alpha_2 - \alpha_1 = \pi/3$ and lower curves separated by $\alpha_2 - \alpha_1 = \pi/3$ to $\alpha_2 - \alpha_1 = 2\pi$. Scattering angle shown is at $(\theta_k, \phi_k) = (\pi/4, 3\pi/4)$.

tronic labels in diatomics or vibration-rotation states in polyatomics), but application of the theory only requires technical extensions which we have described previously for the two-laser case.^{2b} Finally, note that polarization control disappears entirely if one examines the total photodissociation cross section.

In summary, photodissociation with variable elliptical polarization provides a direct route to the experimental demonstration of control of product populations through

phase-controlled excitation of pure states. Quantitatively, such control has been shown to be substantial and hence experimentally demonstrable in both M -selected and M -averaged cases.

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⁷H. Werner and W. J. Meyer, *Chem. Phys.* **74**, 5802 (1981); C. A. Asaro and A. Dalgarno, *Chem. Phys. Lett.* **118**, 64 (1985). LiF itself is of little interest here since the ion/atom ratio in photodissociation by linearly polarized light varies over a range close to 0-1 as one scans the angular distribution. However, the LiF potentials provide a useful starting point for the construction of physically reasonable models.

⁸Computations on such systems are ongoing (M. Shapiro and P. Brumer, to be published).