

Interference between Optical Transitions and Control of Relative Cross Sections

In a recent Letter, Chen, Yin, and Elliott¹ showed that the probability of ionization can be altered by varying the relative laser phase in the simultaneous five-photon and three-photon excitation of Hg. This result provides an important experimental demonstration of the utility of pure quantum interference in altering this process. It also provides the first laboratory demonstration of an experimental scenario² based upon a general principle for controlling atomic and molecular processes termed³ coherent radiative control. Other experimental scenarios based upon the same interference principle include one-photon photodissociation of a superposition state^{3(a)-3(c)} with applications to currents in semiconductors,^{3(d)} pulse-pulse schemes for both unimolecular and bimolecular processes,^{3(f),3(i)} and variable-elliptic-polarization control of differential cross sections.^{3(j)} In all cases the theory suggests generalizations of the experiment of Chen, Yin, and Elliott¹ to systems with multiple product channels.

The purpose of this Comment is to computationally demonstrate that the molecular multiple-product-channel generalization of the experiment of Chen, Yin, and Elliott¹ affords the prospect of a vast range of experimental control over the ratio of total product cross sections (i.e., the relative yield of products). The computation presented below is based upon our previous³ formal treatment and provides the first numerical evidence that interfering optical excitation paths allow for enormous control over total cross sections in photodissociation from stationary states.

Specifically, consider simultaneous one- and three-photon excitation ($\omega_3 = 3\omega_1$) of IBr to produce $I(^2P_{3/2}) + Br(^2P_{3/2})$ and $I(^2P_{3/2}) + Br^*(^2P_{1/2})$. Reliable potential surfaces and coupling strengths⁴ were used in conjunction with the artificial channel method⁵ to produce accurate one- and three-photon photodissociation amplitudes. These were then appropriately combined³ to produce the overall dissociation probabilities. As an example consider photodissociation from the ground vibrational state of $X^1\Sigma_0^+$ with rotational quantum number $J=1$ using $\omega_1 = 6657.5 \text{ cm}^{-1}$, $\omega_3 = 3\omega_1$. Excitation with either of the two frequencies, with electric-field amplitudes $\bar{\epsilon}_3$ and $\bar{\epsilon}_1$, independently produces predominantly ($> 70\%$) $I + Br^*$. The results of simultaneous photodissociation with both frequencies is shown as a contour plot of constant yield (i.e., Br^* probability divided by $Br^* + Br$ probability) in Fig. 1. Here the figure axes are labeled by the amplitude parameter $s = x^2/(1+x^2)$, $x = \bar{\epsilon}_1^3/\bar{\epsilon}_3$, and the relative laser phase $\theta_3 - 3\theta_1$. The results demonstrate extensive control over product yield, the ratio varying from 45% to 95%.

Previous theoretical studies³ have indicated that similar control can be exercised over chemically distinct arrangement channels and over rotational-vibrational distributions within a particular product channel.

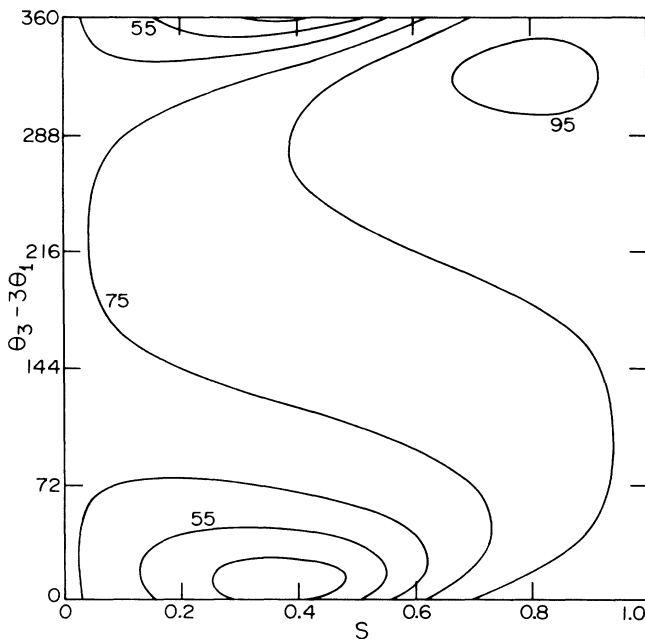


FIG. 1. Contours of constant Br^* vs relative laser amplitude and phase.

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