Identical collision partners in the coherent control of bimolecular reactions

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COMMUNICATIONS

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The coherent control of bimolecular processes typically requires that the system be initiated in a superposition of correlated translational and internal reactant states. We show that by colliding identical molecules one bypasses many of these complexities, allowing for direct studies of coherently controlled collision phenomena. © *2000 American Institute of Physics.* [S0021-9606(00)01930-9]

Coherent control provides a route to controlling reaction dynamics via laser-induced quantum interference effects.[1,2] The vast majority of work has been done on controlling unimolecular processes. However, we recently[3,4] showed that it is possible to apply the principle of coherent control to control bimolecular reactions. These considerations indicate that bimolecular control requires conditions additional to those operative in unimolecular processes, making bimolecular control more challenging. Here we show, however, that reactions of the form $A+A\rightarrow B+C$ afford a unique opportunity for studying controlled bimolecular reactions.

The essential principle of coherent control requires that one create a controllable superposition of degenerate Hamiltonian eigenstates in the center of mass coordinate system.[1] By altering the composition of this superposition, one can alter the ratio of reaction products. Consider then the bimolecular case

$$A+D\rightarrow F+G, \tag{1}$$

where *A, D, F, G* are, in general, molecules of mass M_A, M_D, M_F, and M_G. Here *F* and *G* can be identical to *A* and *D* (nonreactive scattering) or different from *A* and *D* (reactive scattering). We label $A+D$ as arrangement q and $F+G$ as arrangement q'.

In accord with standard scattering theory[5] the cross section $\sigma_E(\mathbf{n},q';\mathbf{m},q)$ for scattering between the incident Hamiltonian eigenstates $|E,q,\mathbf{m};0\rangle$ of $A+D$ (labeled q) and the product Hamiltonian eigenstates $\langle E,q',\mathbf{n};0|$ of $F+G$ (labeled q') is given by

$$\sigma_E(\mathbf{n},q';\mathbf{m},q)=|\langle E,q',\mathbf{n}^-|V_q|E,q,\mathbf{m};0\rangle|^2. \tag{2}$$

Here $\mathbf{n}$, $\mathbf{m}$ denote quantum numbers associated with the reactants and products, respectively, $|E,q',\mathbf{n}^-\rangle$ are the incoming scattering solutions associated with product in state $|E,q',\mathbf{n};0\rangle$, and V_q is the component of the total potential that vanishes as the *A* to *D* distance becomes arbitrarily large. The cross section for scattering into arrangement q', independent of the product internal state $\mathbf{n}$, is then

$$\sigma_E(q';\mathbf{m},q)=\sum_{\mathbf{n}}|\langle E,q',\mathbf{n}^-|V_q|E,q,\mathbf{m};0\rangle|^2. \tag{3}$$

Control of bimolecular collisions is achieved by constructing an initial state $|E,q,\{a_\mathbf{m}\}\rangle$ comprised of a superposition of *N* energetically degenerate asymptotic states $|E,q,\mathbf{m};0\rangle$:

$$|E,q,\{a_\mathbf{m}\}\rangle=\sum_{\mathbf{m}}a_\mathbf{m}|E,q,\mathbf{m};0\rangle. \tag{4}$$

The cross section associated with using Eq. (4) as the initial state, obtained by replacing $|E,q,\mathbf{m};0\rangle$ by Eq. (4) in Eq. (2), is

$$\begin{aligned}\sigma_E(\mathbf{n},q';\{a_\mathbf{m}\},q)&=|\langle E,q',\mathbf{n}^-|V_q\sum_{\mathbf{m}}a_\mathbf{m}|E,q,\mathbf{m};0\rangle|^2\\&=\sum_{\mathbf{m}}|a_\mathbf{m}|^2|\langle E,q',\mathbf{n}^-|V_q|E,q,\mathbf{m};0\rangle|^2+\sum_{\mathbf{m}'}\sum_{\mathbf{m}\neq\mathbf{m}'}a_\mathbf{m}a^*_{\mathbf{m}'}\langle E,q',\mathbf{n}^-|V_q|E,q,\mathbf{m};0\rangle\langle E,q,\mathbf{m}';0|V_q|E,q',\mathbf{n}^-\rangle\\&\equiv\sum_{\mathbf{m}}|a_\mathbf{m}|^2\sigma(\mathbf{n},q';\mathbf{m};q)+\sum_{\mathbf{m}'}\sum_{\mathbf{m}\neq\mathbf{m}'}a_\mathbf{m}a^*_{\mathbf{m}'}\sigma(\mathbf{n},q';\mathbf{m}',\mathbf{m},q),\end{aligned} \tag{5}$$

where $\sigma(\mathbf{n},q';\mathbf{m}',\mathbf{m},q)$ is defined via Eq. (5). The total cross section into arrangement q' is then given by

$$\sigma_E(q';\{a_\mathbf{m}\},q)=\sum_\mathbf{n}\sigma_E(\mathbf{n},q';\{a_\mathbf{m}\},q). \tag{6}$$

Note that Eq. (5), and hence Eq. (6), are now of a standard coherent control form, i.e., direct contributions from each member of the superposition, proportional to $|a_\mathbf{m}|^2$, plus interference terms which are proportional to $a_\mathbf{m}a^*_{\mathbf{m}'}$. It is clear that if we control the $a_\mathbf{m}$, through assorted preparation methods, then we can control the interference term, and hence the scattering cross section. In the case of bimolecular collisions, coherent control arises only from states that are of equal energy and that have the same center of mass momentum.

Consider now the laboratory preparation of the generalized superposition states [Eq. (4)] where for simplicity we limit consideration to a superposition of two states. To emphasize the role of the center of mass motion and the particular utility of choosing $A=D$ we first treat this problem in general (i.e., any D). To do so we examine the scattering of A and D, each in a previously prepared superposition of Hamiltonian eigenstates $|\phi_A(i)\rangle$ and $|\phi_D(i)\rangle$ of molecules A and D. These states are of energy $e_A(i)$ and $e_D(i)$, respectively. We denote $\mathbf{r}_A$ and $\mathbf{r}_D$ as the laboratory position of A and D with $\hbar\mathbf{k}^A$, $\hbar\mathbf{k}^D$ denoting their laboratory momenta. The relative momentum $\mathbf{k}$, relative coordinate $\mathbf{R}$, center of mass momentum $\mathbf{K}$, and position $\mathbf{R}_{\text{c.m.}}$ are defined as

$$\begin{aligned}&\mathbf{K}=\mathbf{k}^A+\mathbf{k}^D,\quad \mathbf{R}_{\text{c.m.}}=(M_A\mathbf{r}_A+M_D\mathbf{r}_D)/(M_A+M_D),\\&\mathbf{k}=(M_D\mathbf{k}^A-M_A\mathbf{k}^D)/(M_A+M_D),\quad \mathbf{R}=\mathbf{r}_A-\mathbf{r}_D.\end{aligned} \tag{7}$$

The wave functions of A and D in the laboratory frame, ψ_A and ψ_D, are of the general form:

$$\psi_A=a_1|\phi_A(1)\rangle\exp(i\mathbf{k}_1^A\cdot\mathbf{r}_A)+a_2|\phi_A(2)\rangle\exp(i\mathbf{k}_2^A\cdot\mathbf{r}_A), \tag{8}$$

$$\psi_D=b_1|\phi_D(1)\rangle\exp(i\mathbf{k}_1^D\cdot\mathbf{r}_D)+b_2|\phi_D(2)\rangle\exp(i\mathbf{k}_2^D\cdot\mathbf{r}_D). \tag{9}$$

The incident wave function is then the product

$$\begin{aligned}\psi_{\text{in}}&=\psi_A\psi_D\\&=[a_1|\phi_A(1)\rangle\exp(i\mathbf{k}_1^A\cdot\mathbf{r}_A)+a_2|\phi_A(2)\rangle\exp(i\mathbf{k}_2^A\cdot\mathbf{r}_A)]\\&\quad\times[b_1|\phi_D(1)\rangle\exp(i\mathbf{k}_1^D\cdot\mathbf{r}_D)+b_2|\phi_D(2)\rangle\exp(i\mathbf{k}_2^D\cdot\mathbf{r}_D)]\\&=\sum_{i,j=1}^{2}A_{ij}\exp(i\mathbf{k}_{ij}\cdot\mathbf{R})\exp(i\mathbf{K}_{ij}\cdot\mathbf{R}_{\text{c.m.}}),\end{aligned} \tag{10}$$

where $A_{ij}=a_ib_j|\phi_A(i)\rangle|\phi_D(j)\rangle$, $\mathbf{k}_{ij}=(M_D\mathbf{k}_i^A-M_A\mathbf{k}_j^D)/(M_A+M_D)$, and $\mathbf{K}_{ij}=\mathbf{k}_i^A+\mathbf{k}_j^D$.

As constructed, Eq. (10) is composed of four independent noninterfering incident states since each has a different center of mass wave vector $\mathbf{K}_{ij}$. However, we can set conditions so that interference, and hence control, is allowed. That is, we require the equality of the center of mass motion of two components, plus energy degeneracy:

$$\begin{aligned}&\mathbf{K}_{12}=\mathbf{K}_{21},\\&\hbar^2k_{12}^2/2\mu+e_A(1)+e_D(2)=\hbar^2k_{21}^2/2\mu+e_A(2)+e_D(1),\end{aligned} \tag{11}$$

with $\mu=M_AM_D/(M_A+M_D)$. Equation (10) then becomes

$$\begin{aligned}\psi_{\text{in}}&=[A_{12}\exp(i\mathbf{k}_{12}\cdot\mathbf{R})+A_{21}\exp(i\mathbf{k}_{21}\cdot\mathbf{R})]\exp(i\mathbf{K}_{12}\cdot\mathbf{R}_{\text{c.m.}})\\&\quad+A_{11}\exp(i\mathbf{k}_{11}\cdot\mathbf{R})\exp(i\mathbf{K}_{11}\cdot\mathbf{R}_{\text{c.m.}})\\&\quad+A_{22}\exp(i\mathbf{k}_{22}\cdot\mathbf{R})\exp(\mathbf{K}_{22}\cdot\mathbf{R}_{\text{c.m.}}),\end{aligned} \tag{12}$$

where the term in the square brackets, due to Eq. (11), is a linear superposition of two *degenerate* states. We therefore expect that the scattering cross section will be comprised of noninterfering contributions from three components with differing $\mathbf{K}_{ij}$, but where the first term allows for control via the interference between the A_{12} and A_{21} terms. The two remaining terms, proportional to A_{11} and A_{22}, are uncontrolled satellite contributions.

For example, if we design the experiment so that $\mathbf{k}_1^A=-\mathbf{k}_2^D$ and $\mathbf{k}_2^A=-\mathbf{k}_1^D$ then $\mathbf{K}_{12}=\mathbf{K}_{21}=0$, and $\mathbf{k}_{12}=\mathbf{k}_1^A$, $\mathbf{k}_{21}=-\mathbf{k}_1^D$, so that the degeneracy requirement [Eq. (11)] becomes

$$\begin{aligned}&\hbar^2(k_1^A)^2/2\mu+e_A(1)+e_D(2)\\&\quad=\hbar^2(k_1^D)^2/2\mu+e_A(2)+e_D(1).\end{aligned} \tag{13}$$

In general, this condition necessitates a method of preparing ψ_A and ψ_D which correlates the internal states $|\phi_A(i)\rangle$ and $|\phi_D(i)\rangle$ with their associated momenta $\mathbf{k}_i^A$,$\mathbf{k}_i^D$ so as to obtain Eq. (13). This requires a considerable extension of currently available experimental techniques. However, the situation simplifies enormously for the case of $D=A$, the subject of this note. Specifically, consider

$$A+A'\rightarrow B+C. \tag{14}$$

Here we have used A' to denote the molecule A, but in a superposition state which is not necessarily the same as A. If we prepare each of the two initial A and A' superposition states from the same molecular bound states, e.g., $|\phi_A(1)\rangle=|\phi_{A'}(1)\rangle$ and $|\phi_A(2)\rangle=|\phi_{A'}(2)\rangle$ then the requirement for conservation of energy in the center of mass [Eq. (11)] becomes

$$\hbar^2(k_{12})^2/2\mu=\hbar^2(k_{21})^2/2\mu. \tag{15}$$

This condition is satisfied for a standard scattering arrangement where $\mathbf{k}_1^A=\mathbf{k}_2^A$ and $\mathbf{k}_1^{A'}=\mathbf{k}_2^{A'}$, since then $k_{12}=|0.5(\mathbf{k}_1^A-\mathbf{k}_2^{A'})|=|0.5(\mathbf{k}_2^A-\mathbf{k}_1^{A'})|=k_{21}$.

This scenario opens up a wide range of possible experimental studies of control in bimolecular collisions. Specifically, we need only prepare A and A' in a controlled superposition of two states (e.g., by resonant excitation of $|\phi_A(1)\rangle$) to produce a superposition with $|\phi_A(2)\rangle$, scatter them, and vary the coefficients in the superposition to affect the reaction probabilities. Control originates in quantum interference between two degenerate states associated with the contributions of $|\phi_A(1)\rangle|\phi_{A'}(2)\rangle$ and $|\phi_A(2)\rangle|\phi_{A'}(1)\rangle$. This is accompanied by two uncontrolled scattering contributions corresponding to the contributions of

$|\phi_A(1)\rangle|\phi_{A'}(1)\rangle$ and $|\phi_A(2)\rangle|\phi_{A'}(2)\rangle$. Control is achieved by varying the four coefficients a_i, b_i, $i=1,2$.

STIRAP[6] provides a natural choice for such state preparation. A particularly promising version is the tripod-STIRAP variant which was recently suggested[7] and experimentally demonstrated.[8] In the tripod-STIRAP scheme, an additional laser couples the intermediate level (through which the initial and final state are radiatively connected via the pump and Stokes laser) with another unpopulated state. Depending on the overlap in time of the interaction of the additional laser with that of the pump and Stokes laser, any coherent superposition of the initial and final state can be created. The system remains in the superposition state after the interaction with the lasers has ceased and the superposition so created is robust, i.e., it is not sensitive to small variations of the laser intensities or the overlap.

The above-described control approach can be generalized to a superposition of N levels in each of the two A and A' reactants. Specifically, choosing all $\mathbf{k}_i^A=\mathbf{k}^A$ and all $\mathbf{k}_i^{A'}=\mathbf{k}^{A'}$ we have

$$\psi_A=\exp(i\mathbf{k}^A\cdot\mathbf{r}_A)\left[\sum_{i=1}^{N} a_i|\phi_A(i)\rangle\right],$$
$$\psi_{A'}=\exp(i\mathbf{k}^{A'}\cdot\mathbf{r}_{A'})\left[\sum_{j=1}^{N} b_j|\phi_A(j)\rangle\right]. \tag{16}$$

The scattering wave function is then

$$\psi_{\text{in}}=\psi_A\psi_{A'}=\exp(i\mathbf{K}\cdot\mathbf{R}_{\text{c.m.}})\exp(i\mathbf{k}\cdot\mathbf{R})\left[\sum_{i=1}^{N} a_i|\phi_A(i)\rangle\right]\times\left[\sum_{j=1}^{N} b_j|\phi_A(j)\rangle\right]. \tag{17}$$

Since $M_A=M_{A'}$, $\mathbf{k}=(\mathbf{k}^A-\mathbf{k}^{A'})/2$ and $\mathbf{K}=\mathbf{k}^A+\mathbf{k}^{A'}$. The kinetic energy $k^2/2\mu$ is the same for each term in Eq. (17) so that degenerate states in the center of mass frame correspond to states $|\phi_A(i)\rangle|\phi_{A'}(j)\rangle$ in Eq. (17) which are of equal internal energy $e_A(i)+e_{A'}(j)$. Expanding the product in Eq. (17) gives N^2 terms, N terms of which are of differing energy $2e_A(i)$, $i=1,...,N$ and (N^2-N) states of energy $e_A(i)+e_{A'}(j)$, $i\neq j$. Of the latter terms, each is accompanied by another term of equal energy [i.e., $e_A(i)+e_{A'}(j)=e_A(j)+e_{A'}(i)$]. Hence the N^2 terms are comprised of N direct terms plus $(N^2-N)/2$ degenerate pairs which are a source of interference, and hence control. Here control is achieved by altering the $2N$ coefficients a_i, b_i in the initially prepared state [Eq. (17)], e.g., by shaped pulsed laser excitation of $|\phi_A(1)\rangle$ and $|\phi_{A'}(1)\rangle$. The extent to which increasing N affects control must be the subject of further study.

Finally, we note that $OH+OH\rightarrow H_2O+H$ is an excellent candidate for study. Experimentally, this system is desirable because cooled OH has only a few populated rotational levels, the first electronic state (needed in STIRAP) is accessible with conveniently available near-UV radiation, and the H atom product can be detected by resonance enhanced multiphoton ionization, possibly in combination with ion imaging to obtain information of the internal energy of the H_2O product.

Theoretical and experimental efforts to examine this control scenario, with initial applications to isotopes of molecular hydrogen and to $OH+OH\rightarrow H_2O+H$, are under way.

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