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Insights into dynamics of the $F+CD_4$ reaction via product pair correlationJingang Zhou, Jim J. Lin,^{a)} Weicheng Shiu, and Kopin Liu^{b)}*The Institute of Atomic and Molecular Sciences (IAMS), Academia Sinica, P.O. Box 23-166, Taipei, Taiwan 106*

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To unravel the “extra-atom” complexity of the title reaction, we exploit an experimental approach which, by taking advantage of the correlated information of coincident product pairs, allows us to peel off judiciously the intrinsic complications of a six-atom reaction, extracting the underlying backbone of three-atom dynamics. Examining the collisional energy dependencies of the pair-correlated attributes for a given state(s) of CD_3 products from the title reaction, several of major observations can qualitatively be understood, whereas others await further theoretical investigations. An intriguing possibility for the existence of reactive resonances in this six-atom reaction is surmised. © 2003 American Institute of Physics. [DOI: 10.1063/1.1592153]

The field of gas-phase reaction dynamics has reached a level of maturity where the detailed dynamics of a few-body system on a single potential energy surface (PES) is essentially a solved problem.¹ As exemplified from several benchmark three-atom exchange reactions,^{2–8} and soon for a few favorable four-atom reactions such as $OH+H_2\rightarrow H_2O+H$,^{9,10} the exact quantum dynamics can be computed on a highly accurate *ab initio* PES with the results compared very favorably with the most detailed experimental observable, such as the state-to-state differential cross section (DCS). These really represent a remarkable accomplishment of the field for both experimentalists and theoreticians in recent years.

As we move into larger reaction systems, the number of degrees of freedom increases rapidly and the situation becomes far more complex and challenging. For a chemical reaction that forms two molecular products, for example, even if the state-resolved DCS for each product is obtained individually, the coincident attributes of the co-products are still lacking. In a recent report,¹¹ we exploited a new method, which combines the state-specific “tagging” of one product by laser spectroscopic detection with a high-resolution ion imaging technique,¹² to reveal the coincident information of the product pair in a state-correlated manner. The pair-correlation information is more than another layer of details or specificity. It represents, whatever attribute or distribution one is measuring, the joint probability matrix $\mathbf{P}(n_1, n_2)$ for finding a product 1 coincidentally formed in state n_1 when the other product 2 is in state n_2 in the same reactive event. From the viewpoint of the transition-state theory, how a chemical transformation takes place is mostly governed by the transition state property. However, the transition state is

not static, namely, what is relevant are not just the energetics and the structure, etc. It is dynamic in nature, namely, what really counts is the concerted motion of all atoms in the vicinity of the transition state region. It is conjectured that the correlation of coincident product pairs could potentially provide the most revealing imprint of this concerted motion in the transition state region.

Because the correlation information $\mathbf{P}(n_1, n_2)$ is $n_1 \times n_2$ in dimension, it can be significantly larger than the sum of the uncorrelated information, $n_1 + n_2$. Moreover, the $\mathbf{P}(n_1, n_2)$ represents only the encoded information which must be decoded to be insightful. The most pressing issue, once the correlated information is available, becomes how to sort the order out of chaos or how to digest these enormous amounts of correlated information. In view of many useful concepts prevailed over the past thirty years for a typical $A+BC$ reaction,¹³ we seek a hierarchical approach that enables us to differentiate those attributes, which can be comprehended from the extension of the $A+BC$ lesson, from those remained, which could arise from the intrinsic “extra-atom” complexity of a polyatomic reaction.

In this Communication we report our first step toward understanding the dynamics of the reaction $F+CD_4\rightarrow DF+CD_3$. Our recent crossed-beam experiments^{14,15} indicated that the reaction exhibits a threshold of ~ 0.5 kcal/mol, and up to $E_c=8.5$ kcal/mol only the v_2 -mode (the umbrella motion) excitation of the CD_3 product has significant populations. Using a newly-developed, time-sliced ion velocity imaging technique,¹² we were able to reveal the state-correlations of the coincident product pairs of $CD_3(0v_200)$ and $DF(v')$ at one collision energy $E_c=5.37$ kcal/mol, which show striking differences.¹¹ Obviously, this information involves the quantum structures of both products, and the CD_3 product is not merely a spectator.

To unfold the complexity, we now turn our focus into the correlated DF attributes for a given CD_3 state(s) and examine

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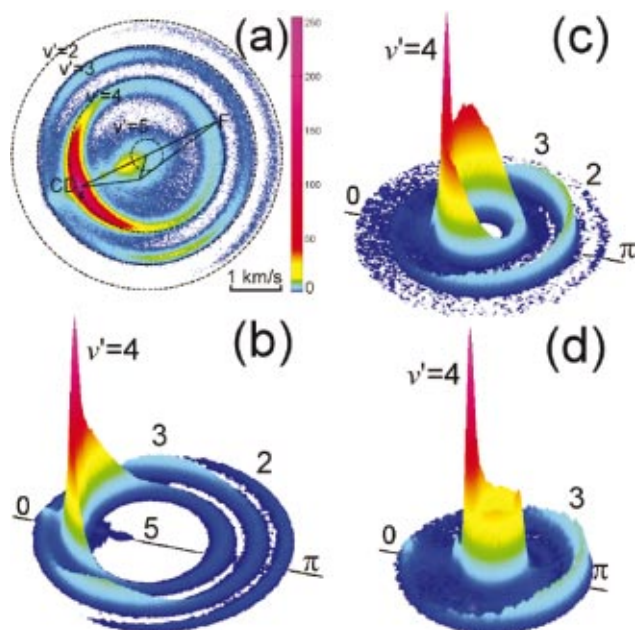


FIG. 1. (Color) (a) Raw image of the state-selected CD_3 products from the $\text{F} + \text{CD}_4 \rightarrow \text{DF} + \text{CD}_3$ reaction at $E_c = 8.36$ kcal/mol. The successive ring features correspond to the labeled vibrational states of the coincident DF product. (b) CD_3 product state-resolved flux-velocity contour maps derived from (a). The density-to-flux correction has been made. The intensity has been weighted by u^2 in accordance with conventional representation of the doubly differential cross section [$d^2\sigma/du d(\cos\theta)$]. (c) and (d), as (b) but for $E_c = 2.77$ and 1.48 kcal/mol, respectively.

their dependencies on collision energies. By keeping the structural factor of the CD_3 product unchanged, CD_3 is then regarded as a pseudospectator so that the situation mimics more closely the familiar three-atom reaction. In other words, an experimental approach to reduce the dimension was adapted, which allows the dynamical attributes thus obtained for the present six-atom reaction to be approximated as a light-atom (D-atom) transfer between two heavy particles (F and CD_3), namely, a heavy–light–heavy system. By setting the probe laser frequency at the peak of the Q branch of the 0_0^0 band, we chose the $\text{CD}_3(0000, \langle N \rangle = 4 \pm 3)$ states in this report because they represent a significant fraction of the overall reactivity of $\text{F} + \text{CD}_4$ from our previous studies.¹⁵ Similar experiments on collisional energy dependencies for the vibrationally excited CD_3 products were also measured and will be reported in the future.

Figure 1(a) shows a representative raw image for $E_c = 8.36$ kcal/mol. The image was acquired in the same manner as that reported recently.^{11,12} Four ringlike structures are clearly visible. Overlaid on the image is the velocity-vector diagram of the collision system, which is based on the well-established energetics of this reaction. The successive rings can be unambiguously assigned to the correlated vibration states (v') of the DF co-products, starting from $v' = 5$ for the innermost feature to $v' = 2$. The clear separation of these rings indicates unequivocally the low rotational excitation of the DF product. Using the same data analysis procedure,¹² the resulted CD_3 product flux-velocity contour map is shown in Fig. 1(b), which represents the doubly differential cross section ($d^2\sigma/du d(\cos\theta)$) of the product pairs in the center-of-mass (c.m.) polar coordinate (u, θ). Similarly, the resulted

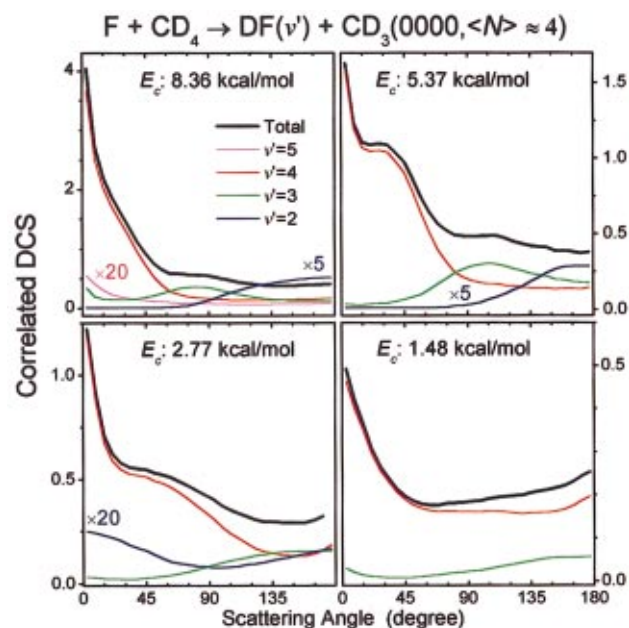


FIG. 2. (Color) Summary of the state-resolved, pair-correlated angular distribution (CDCS). The result for $E_c = 5.37$ kcal/mol (from Ref. 11) is included for comparisons. The scales of the four panels are normalized according to the excitation function for $\text{CD}_3(0000)$ shown in Ref. 15. The black lines represent the vibration-resolved angular distribution of CD_3 products.

contours for the two lower collision energies are shown in Figs. 1(c) and 1(d), respectively. Seemingly counterintuitive is the observation that the harder (i.e., the higher energy) the collision is, the colder the vibrational distribution of the correlated DF product becomes.

More quantitative information can be obtained through the analysis of the contours. The clear separation of the vibrational features makes it easy, and the resultant correlated-DCSs (CDCS) are depicted in Fig. 2 along with that previously reported at $E_c = 5.37$ kcal/mol (Ref. 11) for comparisons. Integrating all angles for each individual CDCS yields the pair-correlated vibrational branching ratio, as summarized in Table I. Apparently, the relative branching ratio of the two dominant vibrational states, ($v' = 4$)/($v' = 3$), decreases with the increase in collision energy—a trend was mentioned above. From the vibrational branching ratios and the flux-velocity contours shown in Fig. 1, the complete energy disposal in coincidence with the formation of $\text{CD}_3(0000, \langle N \rangle \approx 4)$ is obtained (Table I). Despite the sig-

TABLE I. Correlated vibrational branching ratios and energy disposal into $\text{DF}(v') + \text{CD}_3(0000, \langle N \rangle \approx 4)$ products. Note: All energies are in kcal/mol, and $\sigma_{\text{rel}}(E_c)$ is from Ref. 15.

E_c	1.48	2.77	5.37	8.36
DF $v' = 5$	—	—	—	0.007
4	0.87	0.79	0.65	0.58
3	0.13	0.20	0.33	0.36
2	—	0.01	0.02	0.057
$\sigma_{\text{rel}}(E_c)$	0.41	0.85	1.21	1.33
$\langle E_{v'} \rangle_{\text{DF}}$	30.7	30.0	28.8	28.2
$\langle E_R \rangle_{\text{DF}}$	0.12	0.67	1.1	1.4
$\langle E_T \rangle$	1.3	3.0	6.3	9.8

nificant variation in the vibrational branching ratios with collision energies, the averaged energy disposal into the DF co-products, $\langle E_{v'} \rangle_{DF}$, shows rather minor changes. More notable is the observation of the propensity of T (or E_c) $\rightarrow T'$. For a heavy–light–heavy collinear reaction, the (mass-weighted) skew angle¹³ is small (for the present reaction $\beta = 25.5^\circ$), a strong inertial coupling between the two scaled coordinates is anticipated, which in turn leads to the Polanyi's rule¹⁶ that the reagent translation in excess of the barrier to reaction is channeled principally into product translation. Hence, the observed propensity of $T \rightarrow T'$ has a simple kinematic origin. It is remarkable from Table I how well the extend of $T \rightarrow T'$ holds.

By conservation of energy, $E_{\text{total}} = \Delta H_{\text{rx}} + T = V_{CD_3} + R_{CD_3} + V_{DF} + R_{DF} + T'$. Since $T \rightarrow T'$ and both V_{CD_3} and R_{CD_3} are preselected by laser detection, $V_{DF} + R_{DF}$ is necessarily invariant to the change in collision energies. As will be argued later, R_{DF} is expected to be small. Hence, most of reaction exoergicity will be deposited into the vibration of the DF co-product. Again, this is anticipated for an exoergic reaction with an early barrier, in particular for a system with small skew angle. On the other hand, the quantitative vibrational distribution of the DF co-product must originate from detailed dynamics, thus depending on the actual PES. We noted in passing that the observed propensity of $T \rightarrow T'$ is intimately connected to the previously proposed conservation of vibration action of the two vibrators, DF and CD₃.¹¹

The conservation of angular momentum dictates that $\mathbf{I} \approx \mathbf{J} = \mathbf{N}_{CD_3} + \mathbf{j}_{DF} + \mathbf{I}'$. (The initial rotational angular momentum of CD₄ is negligibly small for a supersonic expansion beam.) For a light-atom transfer reaction, both the initial and the final orbital angular momenta (\mathbf{I} and \mathbf{I}') are mainly carried by the orbiting motion of the two heavy particles. The reaction of F+CD₄ is fast,¹⁷ and is believed to proceed through a predominantly linear transition-state in the F–D–C geometry.¹⁸ As demonstrated by Schulten and Gordon¹⁹ for many direct, three-atom reactions with heavy–light–heavy mass combination, \mathbf{I} contributes mostly to \mathbf{I}' , and for a nearly collinear reaction often $\mathbf{I} \approx \mathbf{I}'$, i.e., a coplanar dynamics. The estimated \mathbf{I} for the title reaction ranges from about $100\hbar$ to $\geq 200\hbar$ over the energies of this study. The probed N_{CD_3} has been locked to low values, the angular momentum constraint leads naturally to small values of j_{DF} , thus, small R_{DF} , as evidenced from the clear separation of the rings.

The above kinematic constraint on angular momenta, $\mathbf{I} \approx \mathbf{I}'$, could also have important implication on the observed total angular distributions (Fig. 2, black lines). In general, for a long-lived complex-forming reaction, the exact shape of angular distribution can reveal the degree of correlation between reactant and product angular momenta. For example, the observation of sharp forward–backward symmetry in the c.m. angular distribution implies $\mathbf{I} \approx \mathbf{I}'$ and an isotropic angular distribution will suggest $\mathbf{I} \approx \mathbf{j}'$.^{20,21} In the case of a direct elementary reaction which does not proceed through a long-lived complex, the form of the c.m. angular distribution reveals the favored reactant geometry,¹³ providing insights into the angular dependence of the PES. For example, a bend approach or a softer bending potential could lead to substan-

tially more sideways and forward scattering of products. Nevertheless, the above correlation between angular distribution and angular momentum disposal remains largely valid even for a direct reaction. And the sharpness of forward or backward peak is also likely to indicate how closely the orientation of \mathbf{I}' lies parallel or antiparallel to that of \mathbf{I} . In this sense, the observation of a sharp forward feature for the present reaction over a wide range of collision energies has its kinematic root, at least partially, from $\mathbf{I} \approx \mathbf{I}'$.

A closer inspection of total angular distributions also reveals a small backward peak for the two lower energies. Moreover, the ratio of (forward peak)/(backward peak) decreases monotonically with the decrease in collision energy. Both aspects are qualitatively in line with the expectation of the osculating complex model for reaction.²² The possibility of the involvement of a short-lived complex in this reaction is not too surprising in view of the mass combination and intrinsic time scales: The reaction time is governed by the slower trajectory of two heavy particles, whereas the faster chattering-motion of the light atom manifests itself as a transient complex. An interesting question then arises: Does there exist any quasibound state or reactive resonance in this reaction? or is the state-specific sharp forward peak the manifestation of a simple (transition-state) threshold effect?²³ In light of the similar mass combination and energetics of the present reaction to those of F+HD \rightarrow HF+D in which a reactive resonance has recently been demonstrated,^{6,7} the above question is perhaps not too far-fetched.

In that regards, one should also keep in mind an alternative viewpoint about the total angular distribution. Since $T \rightarrow T'$, this reaction is on average like an elastic scattering. Aside from the rainbowlike feature near 30° – 45° (Fig. 2), the total angular distribution indeed appears reminiscent of that of a hard-sphere collision.²⁴ (In this viewpoint, the rainbowlike features could arise from the van der Waals well, analogous to the elastic rainbow.) For a hard-sphere elastic scattering, it is well known that the quantum calculation yields a sharp forward peak superimposed on an isotropic angular distribution. The classical version will be just the isotropic component. This sharp forward peak is essentially geometric in nature resulting from the difference in impact times with different portions of the hard sphere. In other words, it is a consequence of interference phenomena and doesn't invoke any trapping of quasibound states nor the threshold effect. Nevertheless, time delay is a common characteristic of all three mechanisms: a quasibound or trapped state, a reactive threshold effect, and a hard sphere scattering.^{23–26} The time delay allows the collision partners to rotate before forming the products, thus could yield a forward peak in angular distribution. Again, like the correlated vibrational branching ratio, the more detailed CDCS will depend sensitively on the PES.

In summary, by “tagging” a specific group of CD₃ product states and examining the collisional energy dependencies of thus correlated attributes of the DF coproduct, we elucidated in this study how to experimentally decompose a complex reaction problem into simpler pieces that preserve the essential physics. Several well established concepts from the

simple A+BC reaction were drawn to gain insights into the present six-atom system. The three-atom dynamics revealed here could serve as the underlying backbone to decipher the “extra-atom” complexity when more detailed topography of PES becomes available. Three possible mechanisms were speculated for the origin of the sharp forward peak. The possibility of the existence of reactive resonance in this polyatomic reaction is intriguing, and deserves further investigations.

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