

**Rotationally selected product pair correlation in  $F + CD_4 \rightarrow DF(v) + CD_3(=0, N)$**

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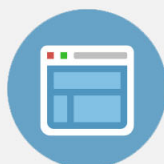
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## Rotationally selected product pair correlation in $F + CD_4 \rightarrow DF(\nu') + CD_3(\nu=0, N)$

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The title reaction was studied in a crossed-beam experiment by imaging of state-selected products. The rotational state selection of the  $CD_3$  products was achieved using  $(2+1)$  resonance-enhanced multiphoton ionization. The coincident information on the DF coproducts was revealed in a state-resolved manner from time-sliced velocity map images. Significant dependences of both the correlated differential cross sections and the DF vibrational branching ratios on the “tagged”  $CD_3$  rotation states were found. The dynamical implications of one of the major findings are discussed.  
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In a series of recent reports, we applied a newly developed, time-sliced ion velocity imaging technique<sup>1</sup> to obtain the state-specific correlation of coincident product pairs in the  $F + CD_4$  (Refs. 2 and 3) and  $F + CHD_3$  (Ref. 4) reactions. Experimentally, a  $(2+1)$  resonance-enhanced multiphoton ionization (REMPI) technique was used to ionize the methyl radical products.<sup>5</sup> The frequency of the laser was either fixed at the peak<sup>1–4</sup> or scanned back and forth over the  $Q$  head<sup>6</sup> while acquiring ion images. In the course of these investigations, we observed some subtle differences in results, depending on whether the laser frequency was scanned or not. Tentatively, we ascribed it to the dependence on the rotational states of the methyl radicals being sampled.<sup>2</sup> The ascription is, however, somewhat uncertain in view of the comparably small rotation constant [ $B \approx 4.8 \text{ cm}^{-1}$  for  $CD_3$  (Ref. 7)] and relatively low rotation population of  $CD_3$  products.<sup>5</sup> Reported in this paper is direct verification of such rotational effects, which in turn demonstrates the active role of the  $CD_3$  rotor in this reaction.

Figure 1 presents the  $(2+1)$  REMPI spectrum around the  $0_0^0$  band of the  $CD_3$  product from the  $F + CD_4$  reaction at  $E_c = 5.37 \text{ kcal/mol}$ . The very intense, central feature is the  $Q$  head, which was used in our previous studies.<sup>1–4,6</sup> The small spectral features on both sides are the  $N$ -resolved peaks of the  $O$ ,  $P$ ,  $R$ , and  $S$  branches, respectively. As is seen, the intensities of those  $N$ -resolved peaks are, using linearly polarized light, generally weaker than the  $Q$ -head signal by 1–2 orders of magnitude. To uncover the  $N$  dependence of the pair-correlated attributes, we tuned the laser frequency to the peak of the  $N$ -resolved feature<sup>8</sup> and acquired the ion image at 20 Hz for 2–3 h, accumulating to about  $2\text{--}3 \times 10^5$  ion events.

Exemplified in Fig. 2(a) is one of the raw images. The REMPI laser was parked at the  $S(3)$  transition—i.e., probing the  $N=3$  state. Distinct ring features are clearly displayed.

Nearly identical images were obtained for the two experimental configurations: the linear polarization of the probe laser lied either parallel or perpendicular to the initial relative velocity vector of the collision system. We therefore concluded no rotational alignment effects (in the collision frame) of the results.

Overlaid on the image is the Newton diagram of the collision system; thus, the coincidentally formed DF vibrational states are readily assigned. After the density-to-flux transformation,<sup>1</sup> the desired product velocity–flux contour map can be obtained and is presented in Fig. 2(b) in a three-dimensional representation. Similarly, the contour maps for  $N=5$  and 9, when the transitions of  $O(5)$  and  $O(9)$  were probed, are depicted in Figs. 2(c) and 2(d), respectively. All three contour maps exhibit three ringlike structures corresponding to the coincidentally formed DF in  $\nu' = 4, 3,$  and  $2$ , respectively. Yet the appearances of those correlated attributes are significantly different.

The product velocity–flux contour maps shown in Figs. 2(b)–2(d) represent the correlated doubly differential cross

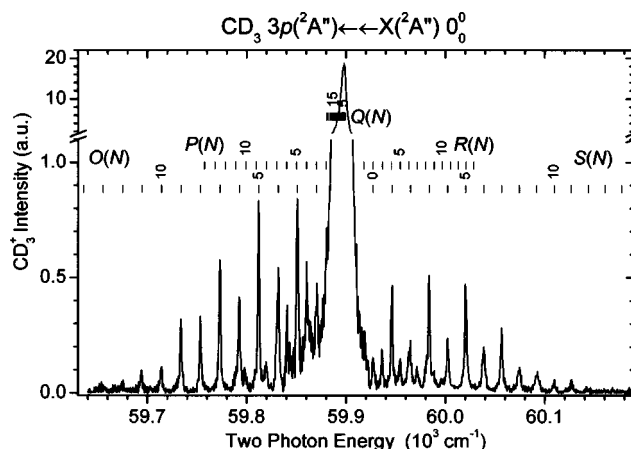


FIG. 1.  $(2+1)$  REMPI spectra of the vibrational ground state of  $CD_3$  products from the title reaction at  $E_c = 5.37 \text{ kcal/mol}$ . A linearly polarized laser was used. The very intense, central peak is the  $Q$  head. The much weaker,  $N$ -resolved  $O$ ,  $P$ ,  $R$ , and  $S$  branches are indicated.

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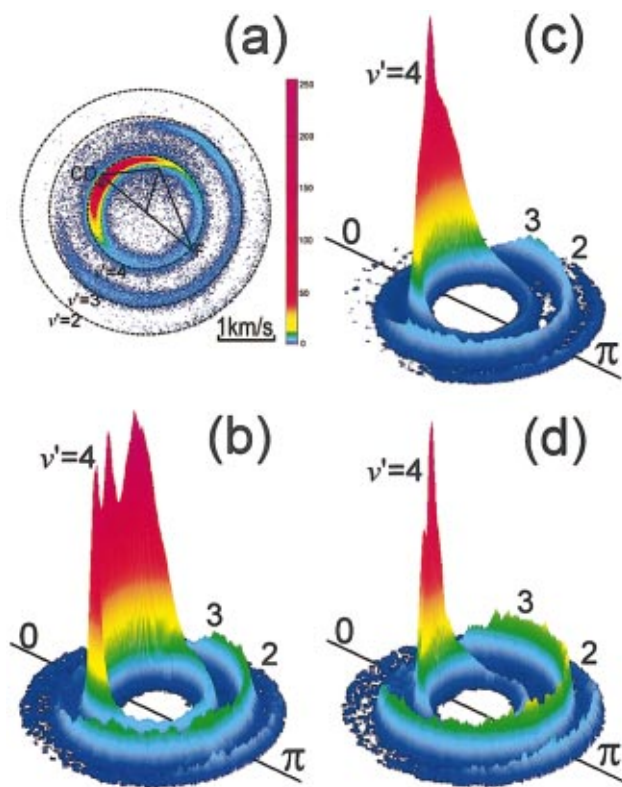


FIG. 2. (Color) (a) A typical raw image when the  $S(3)$  transition was probed. (b) The resultant product velocity-flux contour map,  $d^2\sigma/d\mu d(\cos\theta)$ , derived from (a) when  $CD_3$  ( $\nu=0, N=3$ ) is interrogated. (c) and (d), similarly to (b) for  $CD_3$  ( $\nu=0, N=5$ ) and  $CD_3$  ( $\nu=0, N=9$ ), respectively. The intensities of the three contours are not normalized to one another.

sections (DCSs)  $d^2\sigma/d\mu d(\cos\theta)$ .<sup>9</sup> Integrating over the relative product speed  $\mu$  within the range of a specific ring yields the vibrationally state-resolved angular distribution of the DF products in coincidence with the “tagged”  $CD_3$  rovibrational state. The resultant correlated DCSs for the tagged  $CD_3$  states,  $N=3, 5$ , and  $9$ , are depicted in Fig. 3. The dependences on  $N$  are indeed striking, *indicative of the active role of the  $CD_3$  rotor in this reaction*. For all three  $N$  states, the correlated DF ( $\nu'=4$ ) states feature a sharp forward angular distribution superimposed on an isotropic component. In addition, a rainbowlike feature in the small scattering angles prevails with the decrease in  $N$  quantum numbers. The correlated DF ( $\nu'=3$ ) states are predominantly backward/sideways scattered, though the protrusion into the forward hemisphere is seen for  $N=9$ . The coincidentally formed DF ( $\nu'=2$ ) states are essentially characterized by backward scatterings for all three  $N$  states. Compared to those reported previously (Ref. 2, Fig. 3) in which the probe laser was tuned to the peak of the  $Q$  head—namely,  $\langle N \rangle \approx 4$ —it is gratifying to note the excellent consistency between those correlated DCSs and the present ones for  $N=3$  and  $5$ .

The right lower panel summarizes the correlated angle-dependent energy disposal. The fractional energy disposed into the coincident DF rotor is always small and nearly independent of both the scattered angles and  $N$  states. As a result, the angular dependences of the two remaining degrees of freedom,  $f_{V(DF)}$  and  $f_T$ , form a mirror image. The fact

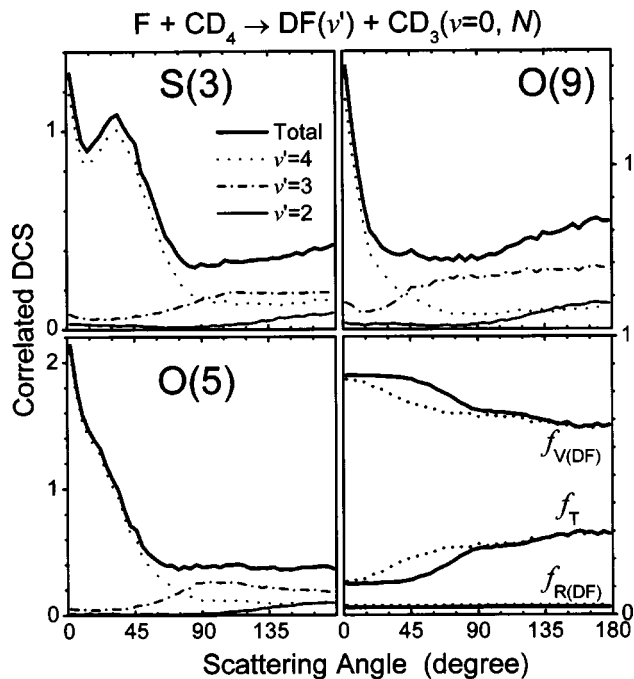


FIG. 3. Summary of the state-resolved, pair-correlated angular distributions (CDCS). The scales of the three panels—i.e., the left two and the right upper one—are normalized to the  $CD_3$  ( $\nu=0, N$ ) rotation state distribution (Ref. 5). Depicted in the right lower panel are the angular dependences of the correlated energy disposal. The solid lines are for  $N=3$ , and the dotted lines for  $N=9$ . The results for  $N=5$  (not shown) lie in between.

that the rotational motions of the two molecular products (DF and  $CD_3$ ) appear largely uncorrelated is somewhat unexpected (*vide infra*). Intuitively, one might have anticipated some sort of correlation if the two products recoil from impulsive interactions at the transition state.<sup>10</sup> About 75% of available energy is channeled into the vibration of the DF coproduct. Its angular dependency—more DF vibrational excitation in the forward direction than the backward—is reminiscent of the previous finding for the mode-correlated product pairs in the  $F+CHD_3$  reaction when the product  $CHD_2$  states  $4_2$  or  $3_1$  were probed.<sup>4</sup> Again, this could be suggestive of the correlation between the impact parameter and scattered angle for a direct reaction with an early barrier, as detailed in the previous report.<sup>4</sup> The variation between different  $N$  states—the solid line for  $N=3$  and the dotted one for  $N=9$ —can be traced to the rainbowlike feature in the correlated DCS.

Integrating the state-specific correlated DCS yields the correlated DF vibration branching ratio, and Fig. 4(a) summarizes the results. For ready comparisons between different  $N$  states, we normalized the branching ratios for each  $N$  such that their sum is equal to 1. The correlated vibration branching ratios show a quite remarkable dependence on the tagged  $N$  states: the peaking of the distribution changes from  $\nu'=4$  for  $N=3$  to  $\nu'=3$  for  $N=9$ . The vibrational spacing<sup>11</sup> between  $\nu'=4$  and  $3$  is 7.53 kcal/mol and the rotational energy difference between  $N=3$  and  $9$  is merely 1.07 kcal/mol.<sup>7</sup> Yet the product pair of the DF vibrator (not the DF rotor) and the  $CD_3$  rotor appears highly correlated. Viewing this correlation in a different way provides further in-

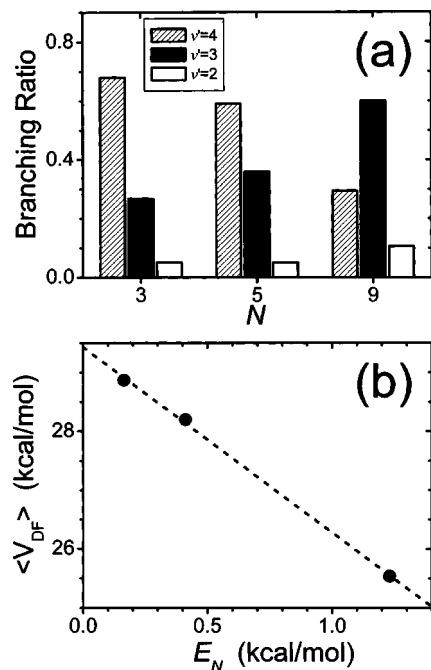


FIG. 4. (a) The correlated vibration branching ratios of the DF coproducts for different  $N$  states of the CD<sub>3</sub> ( $\nu=0$ ) product. (b) The linear anticorrelation between  $\langle V_{DF} \rangle$  and  $E_N$ .

sights. The averaged vibration energy of the DF subensembles  $\langle V_{DF} \rangle$ , which correlates with a specific CD<sub>3</sub> rotation state, can be calculated from the correlated branching. As is shown in Fig. 4(b), a linear anticorrelation between  $\langle V_{DF} \rangle$  and the CD<sub>3</sub> rotational energy  $E_N$  is found with a slope of  $-3.2$ . This is to be compared with the anticorrelation between the two vibrators of this reaction, DF( $\nu'$ ) and CD<sub>3</sub>( $\nu_2$ ), in which a slope of about  $-1.0$  was reported.<sup>2</sup> Apparently, the F+CD<sub>4</sub> reaction proceeds in a way such that the rotation of CD<sub>3</sub> is about 3 times more effective than the CD<sub>3</sub> vibration in compensating the energy disposal into the vibration of the DF coproducts.

It is instructive to examine the implication of this linear anticorrelation between  $\langle V_{DF} \rangle$  and  $E_N$ . In this experiment, the CD<sub>4</sub> beam is cold from supersonic expansion, so its internal energy is negligibly small. By conservation of energy, one has  $E_c - \Delta H_{rx} = E_{V(CD_3)} + E_N + E_{\nu'} + E_{j'} + E_T$ . All symbols in this equation have their usual meanings, and the prime (nonprime) indexes refer to the motions of the DF(CD<sub>3</sub>) products. The vibrational ground state of CD<sub>3</sub> was probed; thus,  $E_{\nu'} + E_N + E_T = -\Delta H_{rx} + E_c - E_{j'}$ . In a very illuminating paper, Schechter *et al.*<sup>12</sup> elucidated kinematic constraints in  $A+BC$  reactive collisions. They argued convincingly that the usual conversion of reactant orbital angular momentum  $\mathbf{l}$  to product rotational angular momentum  $\mathbf{j}'$  for a heavy+heavy–light system<sup>9</sup> should also hold for other mass combination in collinearly dominated reactions due to the steric requirements of the reaction. Hence, one has  $\mathbf{j}' \approx \alpha \mathbf{l}$  under more general conditions, where  $\alpha$  is a dimensionless factor accounting for kinematic constraints.<sup>12</sup> For the present polyatomic reaction of F+CD<sub>4</sub>, the transition state is believed to be nearly collinear in F···D···C geometry.<sup>13</sup> We assume analogously  $\mathbf{j}' \approx \alpha \mathbf{l}$  for the newly formed DF

rotor. Recalling that  $E_{j'} \approx B j'^2$  and  $l^2 = 2\mu b^2 E_c$ , thus  $\langle E_{j'} \rangle \propto E_c$ —i.e.,  $\langle E_{j'} \rangle$  (or  $\langle b^2 \rangle$ ) is nearly independent of the  $N$  states (*vide supra*), which is as we found experimentally (Fig. 3). Moreover, the expression for conservation of energy becomes  $E_{\nu'} + E_N + E_T = \text{const}$ —i.e., invariant to the selected  $N$  states. The linear relationship between  $\langle V_{DF} \rangle$  and  $E_N$  can then be alternatively expressed as  $\langle E_T \rangle \approx C + 2.2E_N$ , where  $C$  represents a positive constant.

The conservation of angular momentum can be written as  $\mathbf{l} = \mathbf{l}' + \mathbf{j}' + \mathbf{N}$ . The assumption of  $\mathbf{j}' \approx \alpha \mathbf{l}$  yields  $(1 - \alpha)\mathbf{l} \approx \mathbf{l}' + \mathbf{N}$ . Squaring it and expressing the terms in the respective energy, one has  $\langle E_T \rangle \approx C_1 E_c - C_2 E_N - C_3 \langle \mathbf{l}' \cdot \mathbf{N} \rangle$ , where the weak  $N$ -dependent parameters have been grouped into three *positive* constants  $C_1$ ,  $C_2$ , and  $C_3$ . Comparing it with the above implied relationship of  $\langle E_T \rangle \approx C + 2.2E_N$ , one is led to that  $\langle \mathbf{l}' \cdot \mathbf{N} \rangle$  is most likely  $N$  dependent and *negative*. In other words,  $\mathbf{N}$  tends to lie antiparallel to  $\mathbf{l}'$ . As argued previously,<sup>3</sup> the present reaction is mainly governed by a coplanar dynamics (in the F···D···C three-atom geometries).<sup>14</sup> Physically, the preferential antiparallel of  $\mathbf{N}$  and  $\mathbf{l}'$  will then imply that the product of CD<sub>3</sub> rotors should be mostly of the tumbling rotation (rather than the spinning rotation). The latter implication is entirely in corroboration of our finding from the rotational state distribution measurement.<sup>5</sup>

With the aid of conservation laws, we suggest that the observed anticorrelation between  $\langle V_{DF} \rangle$  and  $E_N$  implies  $\mathbf{N}$  being preferentially antiparallel to  $\mathbf{l}'$ , which in turn accounts for the previously observed dominance of the tumbling rotation.<sup>5</sup> The driving torque to induce the tumbling motion of CD<sub>3</sub> products, however, must arise from, despite the nearly collinear transition state of this reaction, the interactions and/or even the exchange between the transferred D atom and the other three “passive” D atoms as the two products recede from each other. This signifies the importance of the dynamical motions—i.e., more than just the static aspects—of the transition state in understanding the detailed reaction mechanism, a point that has been emphasized in Refs. 2 and 3.

In summary, taking the F+CD<sub>4</sub> reaction as a prototype, we have previously explored several facets of product pair correlation. Examples include the quantum number correlation between the two product vibrators at a fixed collision energy,<sup>2</sup> the collision energy dependence of the correlated DF attributes for a given CD<sub>3</sub> vibrational state,<sup>3</sup> the mode-correlated behaviors in the F+CHD<sub>3</sub>→CHD<sub>2</sub> ( $\nu_4=2$  or  $\nu_3=1$ )+DF( $\nu'$ ) reaction,<sup>4</sup> and the pair-correlated excitation function in F+CH<sub>4</sub> (Refs. 6 and 15). In this paper we add to the list the rotational aspects of product pair correlation. In the theoretical investigations of the  $X+\text{CH}_4 \rightarrow \text{HX}+\text{CH}_3$  family of reactions ( $X$ : atoms or radicals), CH<sub>3</sub> is often treated as a nonrotating moiety.<sup>16</sup> As demonstrated in this work (Figs. 3 and 4), the rotation of CD<sub>3</sub> is in fact a very active participant in the reaction despite its low excitation. And this conclusion is most clearly revealed through the rotationally selected product pair correlation measurement. Being a symmetric top, the CD<sub>3</sub> rotor is characterized by two rotational quantum numbers  $N$  and  $K$ . At present, the effects of the  $K$  quantum number, the  $N/K$  dependence for a vibra-

tionally excited CD<sub>3</sub>, etc., are not totally clear. Works addressing those questions are in progress. As elucidated here and in the previous reports, the pair-correlation information offers a powerful vehicle to unravel the “extra-atom” complexity in a typical polyatomic reaction. We hope these works will stimulate further theoretical investigations along this line.

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