Reactive Resonance in a Polyatomic Reaction

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In the course of an extensive investigation aimed at understanding the detailed mechanisms of a prototypical polyatomic reaction, several remarkable observations were uncovered. To interpret these findings, we surmise the existence of a reactive resonance in this polyatomic reaction. The reaction of concern is $F + CH_4 \rightarrow HF + CH_3$, and the abnormal attributes were revealed only near the reaction threshold. The discovery of reactive resonance in a polyatomic reaction is more than just an extension from a typical atom + diatom reaction. As shown here, it holds great promise to disentangle the elusive intramolecular vibrational dynamics of transient collision complex in the critical transition-state region.

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Reactive resonance or Feshbach resonance is one of the most fascinating phenomena in chemical reaction dynamics [1–3]. The term "resonance" in this context refers to a transiently formed metastable that is produced while the reaction is taking place. The Born-Oppenheimer approximation, an adiabatic separation of electronic from nuclear motions, plays the pivotal role in our fundamental understanding of chemical reactivity [4]. Within this approximation, a chemical reaction is envisioned as nuclear motions evolving from reagents to products on a Born-Oppenheimer potential energy surface (PES). The existence of reactive resonance can be conceptually traced back to dynamical trapping in wells on the vibrationally adiabatic PES — even when there is no potential well on the Born-Oppenheimer PES. It is a quantum mechanical phenomenon and is dynamical in origin—thus the so-called quantum dynamical or trapped-state resonance. Over the past decades, numerous theoretical predictions have been made for the existence of reactive resonances in a number of elementary chemical reactions, notably of the atom + diatom type [5]. At this point in time, the only conclusive experimental evidence for reactive resonance is for the I + HI system [6] from the photodetachment study of IHI^- and for the crossed-beam scattering experiment of the $F + HD \rightarrow HF + D$ reaction [7,8]. Reactive resonance in a polyatomic reaction is a hitherto unexplored frontier, both theoretically and experimentally.

The experimental discovery of a reactive resonance in the F + CH reaction was made using a rotating-source, crossed-beam apparatus described previously [9–13]. The reaction product CH_3 was interrogated by a 2 + 1 resonance-enhanced multiphoton ionization (REMPI) scheme via the intermediate $3p_z^2A''$ Rydberg state [13]. Exemplified in Fig. 1 are three representative spectra near the 0_0^0 band taken at three different collision energies, E_c. (The conventional spectroscopic notation P_m^n denotes the mode P with m and n quanta of excitations in the electronically ground and excited states, respectively.) The high-energy spectrum displays the normal pattern — a dominant Q branch with rotational-resolved P, O, R, and S branches on either side. As the collision energy decreases, the spectral feature of the 0_0^0 band decreases in intensity, and a new feature of the 1_1^1 band that overlaps with the $P(4)$ line of the 0_0^0 band prevails. At E_c = 0.48 kcal/mol, the intensity of the 1_1^1 band becomes comparable to that of the 0_0^0 band.

Figure 2 summarizes their intensity ratios as a function of the collision energy. As is seen, the signal for the formation of the 1_1 state of CH_3 is significant only at low collision energies. The υ_1 is the symmetric-stretch

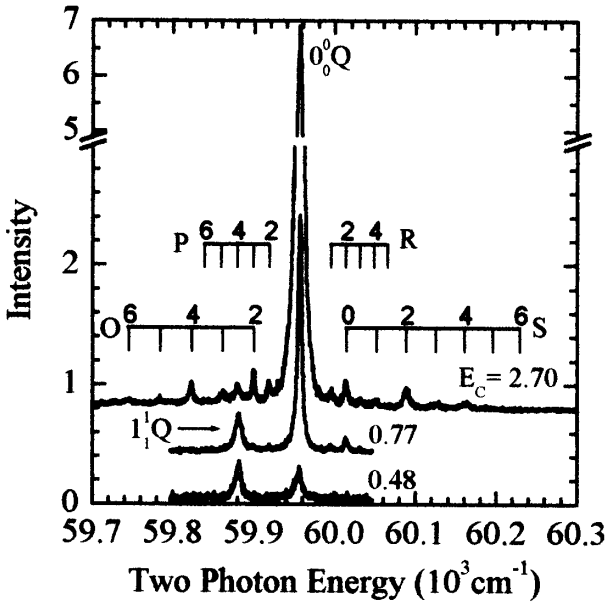

FIG. 1. Three representative 2 + 1 REMPI spectra around the 0_0^0 band of the CH_3 product from the $F + CH_4$ reaction. The rotational features are discernible in high collision energy spectrum. At lower energies, they gradually disappear, indicating less rotational excitation of the CH_3 products, and the 1_1^1 band pops out.

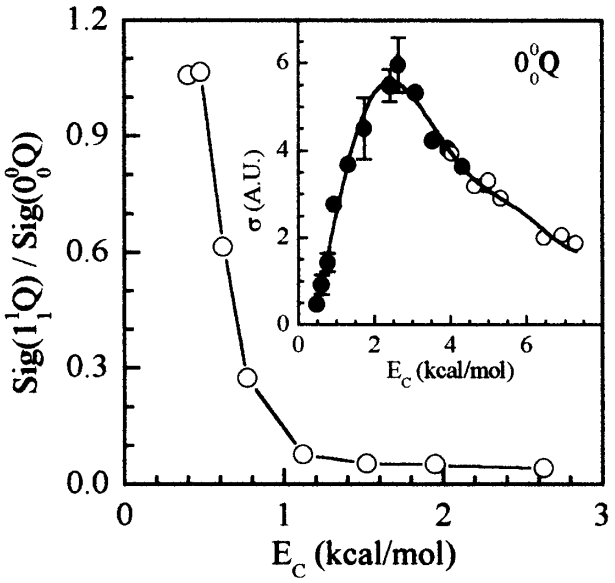

FIG. 2. Summary of the collision energy dependence of the intensity ratios of the 1^1_1 band and the 0^0_0 Q head. Because of the spectral overlap and the opposite energy dependence of the intensities of the 1^1_1 band and the $P(4)$ line of the 0^0_0 band, the actual ratios for $E_c \gtrsim 1.2$ kcal/mol should be smaller than those indicated. The reactive excitation function for the formation of the $CH_3(v = 0)$ is shown in the inset (from Ref. [14]). Combining these two results, the production of $CH_3(v_1 = 1)$ occurs only near the reaction threshold.

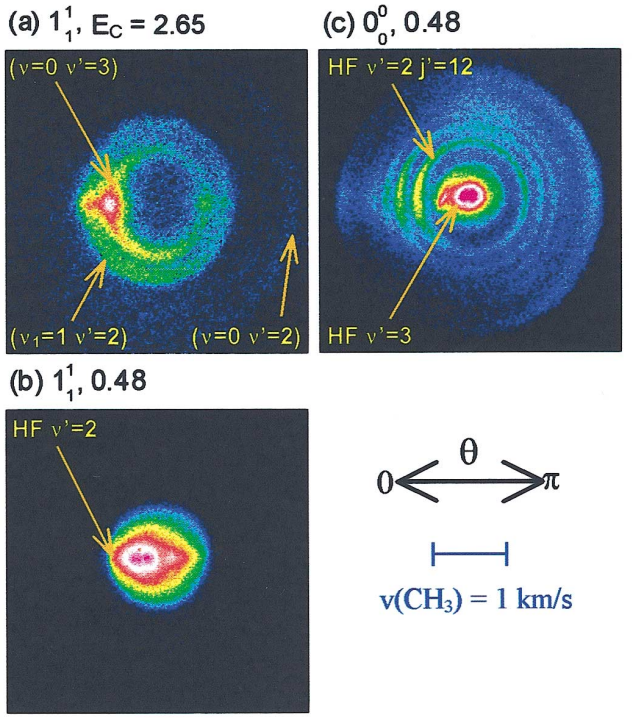

FIG. 3 (color). Three typical product images for illustration. The speed scale and the scattering angle (θ) of the CH_3 product in the center-of-mass frame, and the false-color code of the images are indicated. The images shown in (a) and (b) are for the probe laser frequency set at the peak of the 1^1_1 band. At $E_c = 2.65$ kcal/mol, three ring structures are discernible. Their origins are indicated. At $E_c = 0.48$ kcal/mol, only the feature of the $HF(v' = 2, j') + CH_3(v_1 = 1)$ pair remains. Shown in (c) is the image when the 0^0_0 Q head was probed. The series of ring structures correspond to the rotationally resolved pairs of $HF(v' = 2, j') + CH_3(v = 0)$. The high j' states show more intensities in the forward direction, whereas the low j' states display an opposite preference though a sharp forward peak is also noticeable. The bright spot in the forward direction arises from the molecular beam generated background.

mode with a relatively high harmonic frequency of 3004 cm^{-1} [15]. Its production occurring only near the reaction threshold is counterintuitive and totally unexpected. Also shown in Fig. 2 is the reactive excitation function of the vibrational ground state of the CH_3 product [14]. Combining the two sets of data of Fig. 2 leads to a rapidly declining excitation function for the production of $CH_3(v_1 = 1)$ that peaks at the lowest collision energy of this study—an even more remarkable observation.

To elucidate the underlying mechanism for the observations, we examined the product angular distribution. This was accomplished by using the time-sliced, velocity imaging technique developed recently [9]. Experimentally, the probe laser frequency was fixed at the peak of a spectral band that samples low rotational states of CH_3; the REMPI-generated ions were then velocity mapped, in a three-dimensional sense, onto an imaging detector. Figures 3(a) and 3(b) present the center-sliced images [9] of the 1^1_1 band at $E_c = 2.65$ and 0.48 kcal/mol, respectively. The image at 2.65 kcal/mol shows triple-ring structures. As shown in Fig. 1, at this collision energy both 1^1_1 and the $P(4)$ transition of the 0^0_0 band can contribute spectroscopically. But, the two CH_3 levels should exhibit different energetics in the product image. The weak, outermost ring concentrates in the backward hemisphere. Two inner rings display instead a predominantly forward-peaking feature, though a faint backward peak is also discernible. On energetic ground, the outermost ring is assigned to the formation of the $HF(v' = 2)$ product in concomitance with $CH_3(v = 0, N = 4)$. As to the more intense double-ring structures, the inner and outer features correspond to the correlated product pairs of $HF(v' = 3) + CH_3(v = 0, N = 4)$ and $HF(v' = 2) + CH_3(v_1 = 1)$, respectively. These rings are clearly distinguishable, demonstrating unequivocally low excitations of the coincidently formed HF rotors. The two inner rings dominate the image, reflecting a stunningly high specificity of state correlation in product pairs. At $E_c = 0.48$ kcal/mol, the contribution from the outermost ring vanishes and the production of the $HF(v' = 3) + CH_3(v = 0, N = 4)$ pair is energetically closed. Hence, only the $HF(v' = 2) + CH_3(v_1 = 1)$ pair remains responsible for the observed image, for which a forward-backward asymmetric peaking angular distribution is again noted.

When the laser frequency was shifted to the peak of the 0_0^0 band, the resultant image is displayed in Fig. 3(c) for $E_c = 0.48$ kcal/mol. Far richer features are observed. Energetically, the intense central feature corresponds to the $CH_3(v = 0) + HF(v' = 3)$ product channel, which is endoergic by 0.56 kcal/mol, presumably arising from the small spread of the initial collision energy. The successive ring structures can be ascribed to the coincidently formed rotational states of the $HF(v' = 2)$ coproducts, starting from $j' = 13$ for the innermost ring and outward. As shown in Fig. 4, the correlated rotational population of the $HF(v' = 2)$ coproducts exhibits a broad distribution up to the energetic limit. Moreover, the higher j' states are preferentially scattered in the forward direction, whereas the low j' states favor backward scattering. These striking rotational features persist from threshold up to about 1.3 kcal/mol and diminish at higher collision energies — over much the same energy range as the production of the symmetric-stretch excited methyl radical shown in Fig. 2.

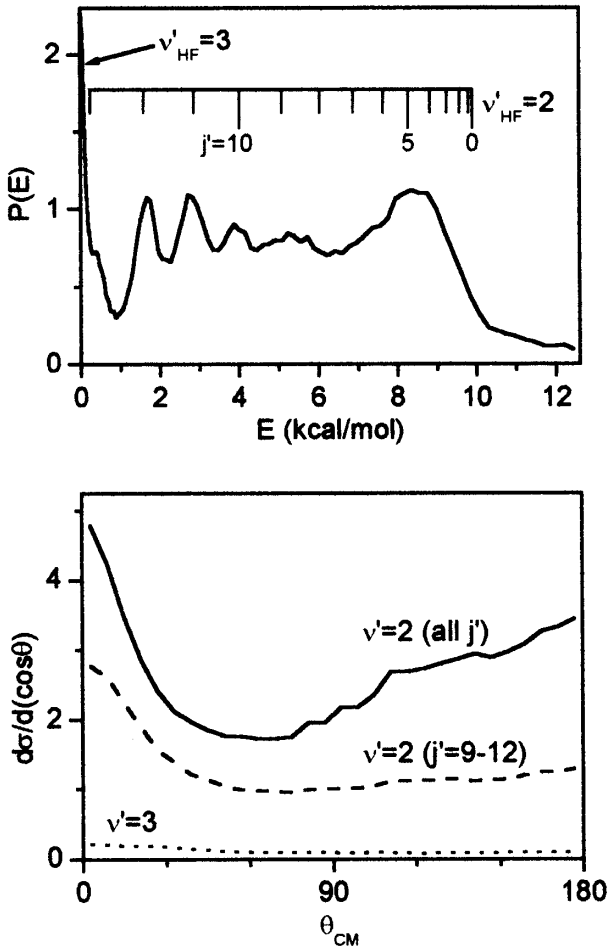

FIG. 4. Product translational energy distribution $P(E) = d\sigma/dE$ and angular distribution $I(\theta) = d\sigma/d(\cos\theta)$ derived from the image shown in Fig. 3(c). Marked on top of the $P(E)$ distribution are the rotational assignments of the $HF(v' = 2, j')$ coproducts. For comparison, the angular distribution for the high-j' states of the HF rotor ($v' = 2$, $j' = 9$–12) is also depicted as the dashed line.

The distinct correlated rotational features revealed in Fig. 3(c) are in sharp contrast to what have been found for this [14] and other isotopic analogous reactions [10–12] at higher collision energies, for which the correlated HF (DF) coproducts are formed with low rotational excitation. Instead, these features are strongly reminiscent of those observed previously for the $F + HD \rightarrow HF(v' = 2, j') + D$ reaction at low collision energies [16,17], for which resonant tunneling has been shown to be the underlying mechanism [7,8]. A similar mechanism is conceived to be operative near the threshold of the present reaction. We further conjecture a quasibound resonance state with the quantum number assignment of three quanta of vibration in the H-F stretch and zeros for all other modes—analogous to the F + HD reaction [7].

At low collision energies where the product channel $HF(v' = 3) + CH_3(v = 0)$ is barely open, the decay of the transient resonance state can proceed via the vibrationally nonadiabatic predissociation (with a rate $1/\tau_p$) into $HF(v' = 2, j') + CH_3(v = 0)$, similar to the F + HD case. Replacing the D atom in HD by a methyl group (CH_3), however, adds extra degrees of freedom. Intramolecular vibrational energy redistribution (IVR) [18] within the resonant complex might then act to open up new decay channels and shorten the resonance lifetime. The v_1-mode excitation of the CH_3 moiety retains the symmetry of collision complex; thus, the coupling between the two vibrationally adiabatic PES's that correlate asymptotically to $HF(v' = 3) + CH_3(v = 0)$ and $HF(v' = 2) + CH_3(v_1 = 1)$, respectively, is symmetry allowed. The energy difference between the two product channels is 1.7 kcal/mol. The anticipated proximity of these two adiabatic surfaces near the transition-state region could give rise to a significant coupling strength. Still, the lifetime of the resonance state has to be sufficiently long for energy exchange between the collective modes of the collision complex to take place so that the formation of $HF(v' = 2) + CH_3(v_1 = 1)$ can compete effectively with the above predissociative decay into $HF(v' = 2, j') + CH_3(v = 0)$. Yet, the fact that only a specific product pair of vibrational mode/state is observed implies a highly restricted IVR process with a rate $1/\tau_{\mathrm{IVR}}$; thus, $\tau_p \sim \tau_{\mathrm{IVR}}$, and the resonant complex must decay into products before energy is completely randomized. In consistency with that, to account for the highly asymmetric forward-backward peaking angular distribution, the resonance lifetime should be significantly shorter than the rotational period (τ_{R}) of the resonant complex [19]; hence, semiquantitatively $\tau_p \sim \tau_{\mathrm{IVR}} < \tau_{\mathrm{R}}$.

At higher collision energies, the vibrationally adiabatic decay of the resonance state into $HF(v' = 3) + CH_3(v = 0)$ dominates, overwhelming the other resonance decay pathways. In addition, the direct recoil mechanism becomes increasingly more important. Consequently, the resonance signatures, which manifest

themselves near threshold as the distinct formations of the forward-scattered high-j' states of HF($v' = 2$) and of the competing product $CH_3(v_1 = 1)$, fade away in experimental observables.

As demonstrated in this work, the ability to image the state-specific correlation of coincident product pairs allows us to elucidate the intricate polyatomic reaction dynamics in a more revealing way, making the present discovery possible. Although any one of these intriguing observations alone provides only a hint, not unequivocal evidence, to the presence of resonance in this reaction, collectively they complement one another to substantiate the claim. The proposed resonance mechanism appears to be the most plausible interpretation to all observations. Future theoretical confirmation is warranted.

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