Analysis on the Signs of Resonances in the F+HCl→HF(v'=3)+Cl Reaction

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＜Introduction＞

The F+HCl(v,j)→HF(v',j')+Cl reaction is a prototypical hydrogen exchange reaction, and belongs to the heavy-light-heavy reaction type which is studied with great interest in molecular dynamics. In this type of reactions, the light atom vibration between the two heavy atoms mediates the formation of meta-stable resonance states. In addition, due to the large exothermic nature of this reaction, the HF molecule results in a highly vibrationally excited state. Therefore, it is expected that these dynamical resonances may appear for this system. However, theoretical analyses on these resonances using theoretical potential energy surfaces have not been performed.

＜Calculation Method＞

For this system, Deskevich et al. have recently calculated an *ab initio* potential energy surface[1] using the full valence MRCI+Q method by taking the complete basis extrapolation using aug-cc-pVnZ basis, where n=2-4 (MOLPRO program[2]). Hayes et al. performed detailed dynamics calculation using this surface[3] (ABC program[4]) and reported the cumulative reaction probability for the J=0 channel.

＜Results＞
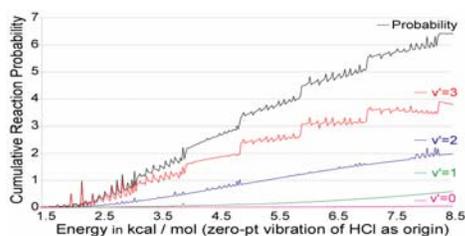
In the figure on the left, we present the calculated cumulative reaction probability (black line) versus the collision energy. In addition to the interesting step feature seen at around 5, 6, and 7 kcal / mol, one is able to recognize the sharp peak structures signifying the existence of resonances. It is expected that these resonances will play a vital role in determining the rate in low collision energies, therefore it is very important to assign these resonances. Furthermore, it can be seen that in the region between 4 to 5 kcal / mol, the peak features disappear. It is of ones interest to understand the origin of this disappearance.

With intent to assign these resonance states, we decomposed the cumulative reaction probability into the contribution from final state vibrational levels. It can easily be noticed that the main contribution for the resonance is coming from the HCl(v=0)+F→HF(v'=3)+Cl channel, with small features coming from the v'=2 channel (at the energies that we are looking at, the channels for HCl(v>1) are closed).

＜Theory & Discussion＞

A three atom reaction for J=0 is expressed using the following Hamiltonian,

$$H = -\frac{\hbar^2}{2\mu_{A,BC}}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_{BC}}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2I}\hat{j}^2 + V(R,r,\gamma),$$

where R, r, γ are reactant or product Jacobi coordinates. The three reactant (product) Jacobi coordinates for the present reaction describe the slow Cl F translational motion (R), the fast HCl (HF) stretching vibration (r), and the HCl (HF) rotation or ClHF bend (γ). Assuming that the fast variable r conserves quantum number (or classical action), we performed the adiabatic separation of this freedom from the other two freedoms; thus, by solving the one-dimensional vibrational equation for a given R and γ, we obtain the adiabatic two-dimensional Hamiltonian (v_r labels the vibrational state)

v=0 reactant Jacobi Coordinate
Adiabatic PES

v'=3 product Jacobi Coordinate
Adiabatic PES
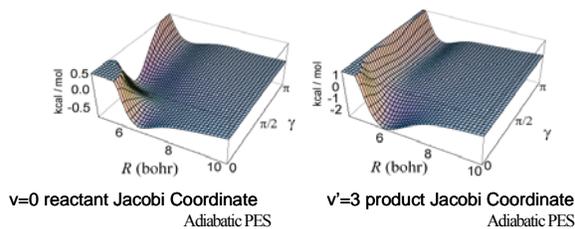
$$H^{v_r} = -\frac{\hbar^2}{2\mu_{A,BC}}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2I}\hat{j}^2 + V^{v_r}(R,\gamma),$$

Since our discussion will be concentrated on the HCl(v=0)+F→HF(v'=3) +Cl channel the respective adiabatic potential energy surface is given in the

figure on the left of the equation. One will easily notice the existence of wells on the adiabatic potential energy surface allowing for the dynamical resonance trappings.
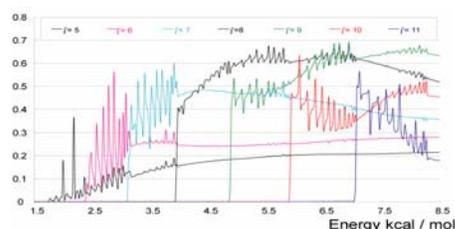
In the figure on the left, we present the separation of the $v'=3$ cumulative reaction probability contribution into their j' state contributions. One of the key points to notice is that the resonance features for a certain energy regime is given from a reaction to a certain j' state in the $v'=3$ product state. Furthermore, the resulting product states are highly excited rotational states, therefore we assume that the rotational motion may be adiabatically separated from the much slower translational motion (R). Thereby giving us a simplified one-dimensional (1-D) Hamiltonian of
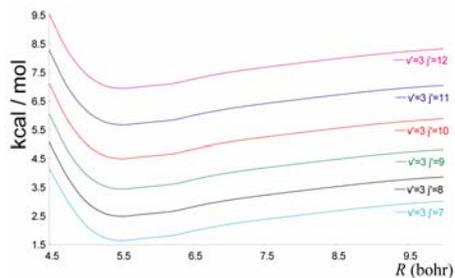
$$H^{v_r j'} = -\frac{\hbar^2}{2\mu_{A,BC}}\frac{\partial^2}{\partial R^2} + V^{v_r j'}(R)$$

$$H^{v_r j'}\left|v_R v_r j'\right\rangle = E^{v_r j'}_{v_R}\left|v_R v_r j'\right\rangle$$

Each resonance state may be assigned using v_R, the quantum number of the 1-D vibrational state on the adiabatic potential curve labeled by v_r and j'(left figure). In the table below, we compare the eigenvalue for a given j' v_R state with the peak positions in the cumulative reaction probability, and one will notice that these peaks are easily assigned, energetically, using this simple model.

resonance j' quanta	resonance v_R quanta	$E^{v_r j'}_{v_R}$ (kcal / mol)	peak (kcal / mol)	Product j' state
7	8	2.89	2.88	6
8	11	3.95	3.91	7
10	4	5.33	5.34	9
11	1	6.02	6.08	10
11	2	6.21	6.22	10
11	3	6.36	6.36	10
12	2	7.48	7.44	11
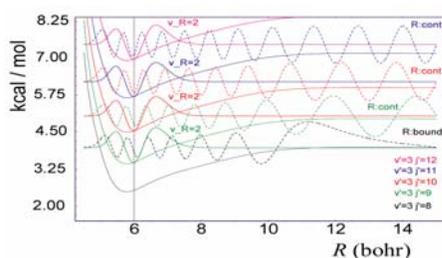
The lowering of one quanta in the j' state seen in going from the resonance state to the product state. This is analogous to the predissociation of van dar Waals complexes. In the figure on the left, we present a simple visualization of this. For a special collision energy, the FHCl molecule gets trapped in the j' potential curve, in a state labeled with a quantum number v_R (the resonance). Then, this bound state (for R) couples with the continuum state (for R) of the j'-1 potential curve causing for the dissociation (e.g. pink to blue, blue to red).

< Conclusion >

Using a simple adiabatic model, the resonance peak structures seen in cumulative reaction probability were assigned using the j' and v_R quantum numbers for the γ and R product Jacobi coordinates. These states mainly couple with the $\Delta j'= -1$ continuum states. We are presently performing wave packet calculations to calculate the life time of these resonances to obtain an understanding on the disappearance seen between 4 to 5 kcal / mol.

< Reference >

1:Deskevich et al. to be published. 2:www.molpro.net. 3:Hayes et al. to be published. 4:Manolopouolos et al. Comput. Phys. Commun. 2000, 133, 128. 5:R. T. Skodje, Annu. Rev. Phys. Chem. 1993, 44, 145.

< Acknowledgement >