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Quasiclassical Trajectory Study of Collisional Energy Transfer between Highly Excited C_6F_6 and N_2 ,O_2 and Ground State C_6F_6

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Abstract: Quasiclassical trajectory calculation (QCT) is used frequently for studying collisional energy transfer between highly vibrationally excited molecules and bath gases. In this paper, the QCT of the energy transfer between highly vibrationally excited C_6F_6 and N_2 ,O_2 and ground state C_6F_6 were performed. The results indicate that highly vibrationally excited C_6F_6 transferred vibrational energy to vibrational distribution of N_2, O_2 and ground state C_6F_6, so they are V-V energy transfer. Especially it is mainly V-V resonance energy transfer between excited C_6F_6 and ground state C_6F_6, excited C_6F_6 transfers more vibrational energy to ground state C_6F_6 than to N_2 and O_2 . The values of QCT , $-\langle \Delta E_{vib} \rangle$ of excited C_6F_6 are smaller than those of experiments.

Keywords: QCT calculation, highly vibrationally excited state, collisional energy transfer.

Collisional energy transfer (CET) between a highly excited molecule and a bath gas plays an important role in many fields of reaction dynamics. Nobuaki Nakashima made the direct experiment on CET between hot C_6F_6 and a series of bath gas[1-3]. H. Hipper did the same experiment later[4]. The results of Hipper are much higher than those of Nakashima only because Nakashima used an inadequate UVA calibration curve. Lenzer simulated the CET between highly vibrationally excited C_6F_6 and single-atomic molecules He, Ar, Xe[5]. His results do not accord with the experimental results very well. Few people did quasiclassical trajectory studies on CET in our country[6-7]. In this paper, the calculation results of the collisional energy transfer between highly vibrationally excited C_6F_6 and N_2 ,O_2 and ground state C_6F_6 are first reported and the mechanisms of these collisional energy transfer are found.

Trajectory Calculations

Intramolecular potential

Intermolecular potential for C_6F_6 see reference 5 for N_2 and O_2 see reference 8 in this paper, we used LJ 12-6 potential with individual atom-atom terms:

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$$V = 4\varepsilon_{x-y}\left[(\sigma_{x-y}/r)^{12} - (\sigma_{x-y}/r)^{6}\right]$$

C_6F_6+N_2： λ_1=1.2734, λ_2=0.4991, $\sigma_{C(F)\text{-}N}$=3.591 Å, $\varepsilon_{C(F)\text{-}N}/k_B$=15.97K,
σ_{eff}=4.966Å , ε_{eff}/k_B=162.71K
C_6F_6+O_2： λ_1=1.216, λ_2=0.5872, $\sigma_{C(F)\text{-}O}$=3.429 Å, $\varepsilon_{C(F)\text{-}O}/k_B$=18.79K,
σ_{eff}=4.836 Å , ε_{eff}/k_B=182.39K
C_6F_6+ C_6F_6： λ_1=1.216, λ_2=0.5872, $\sigma_{C(F)\text{-}C(F)}$=3.429 Å, $\varepsilon_{C(F)\text{-}C(F)}/k_B$=18.79K,
σ_{eff}=4.836 Å , ε_{eff}/k_B=182.39K
The method of obtaining these parameters is in reference 5.

Initial conditions and computational details

Maximum impact parameter b_m is 9 Å collision with N_2 and O_2 or 12 Å collision with C_6F_6. The trajectories were calculated using program MERCURY[9]. The initial center of mass separation was 14 Å collision with N_2 and O_2 or 16 Å collision with C_6F_6 and trajectories were terminated at a distance of 15 Å collision with N_2 and O_2 or 18 Å collision with C_6F_6. The others are same as reference 5.

Results and Discussion

Collision with N_2 and O_2

The results of collisional energy transfer between C_6F_6 and N_2 and O_2 are given in **Table 1**. E′ is initial vibrational energy above zero point energy. $\langle\Delta E_{tot}\rangle$ is total energy transfer per collision. $\langle\Delta E_{vib}\rangle$ is vibrational energy transfer. $\langle\Delta E_{rot}\rangle$ is rotational energy transfer. $\langle\Delta E_{vib}\rangle_{expt}$ is experimental result from reference 2.

First, -$\langle\Delta E_{vib}\rangle$ of highly vibrationally excited C_6F_6 increases with E′, initial vibrational energy of C_6F_6. For example, it is 139cm^{-1} when E′ is 24000cm^{-1} and it is 298 cm^{-1} when E′ rises to 51800cm^{-1} for collision with N_2. This law is consistent with the experimental results.

Second, C_6F_6 transfers more vibrational energy than C_6H_6 when colliding with the same bath gas N_2 or O_2 at same E. The low frequencies in a molecule are thought to govern CET: it has been suggested this is due to low frequencies causing the chattering interactions that characterize energy transfer in polyatomics to “linger longer” and thus transfer more energy[10]. The results are consistent with this conclusion.

Third, the calculated -$\langle\Delta E_{vib}\rangle$ of C_6F_6 is smaller than experimental value. This is similar to collision with Ar in reference 5.

Last, the vibrational energy of C_6F_6 transferred mainly to the vibrational contributions of N_2 and O_2, so they are V-V energy transfers.

Table 1 Energy transfer of C_6F_6 colliding with N_2 and O_2（unit：cm^{-1}）

E′	Molecule	Energy transfer	System			
			C_6F_6+N_2	C_6H_6+N_2*	C_6F_6+O_2	C_6H_6+O_2*
24000	C_6F_6	$-\langle\Delta E_{tot}\rangle$	132±20	43	177±23	49
		$-\langle\Delta E_{vib}\rangle$	139±17	49	187±20	49
		$-\langle\Delta E_{rot}\rangle$	-7	-6	-10	0
		$-\langle\Delta E_{vib}\rangle_{expt}$	488	37	507	44
	Bath gas	$-\langle\Delta E_{tot}\rangle$	-136±10	-122	-169±13	-124
		$-\langle\Delta E_{vib}\rangle$	-116±8	-105	-148±11	-107
		$-\langle\Delta E_{rot}\rangle$	-20	-17	-21	-17
34000	C_6F_6	$-\langle\Delta E_{tot}\rangle$	208±25	54	208±22	53
		$-\langle\Delta E_{vib}\rangle$	219±23	69	231±22	61
		$-\langle\Delta E_{rot}\rangle$	-11	-15	-23	-8
		$-\langle\Delta E_{vib}\rangle_{expt}$	585	44	603	58
	Bath gas	$-\langle\Delta E_{tot}\rangle$	-163±13	-111	-229±58	-117
		$-\langle\Delta E_{vib}\rangle$	-139±10	-94	-207±55	-102
		$-\langle\Delta E_{rot}\rangle$	-24	17	-21	-15
51800	C_6F_6	$-\langle\Delta E_{tot}\rangle$	275±34		342±35	
		$-\langle\Delta E_{vib}\rangle$	298±32		401±37	
		$-\langle\Delta E_{rot}\rangle$	-23		-59	
		$-\langle\Delta E_{vib}\rangle_{expt}$	650		660	
	Bath gas	$-\langle\Delta E_{tot}\rangle$	-183±17		-214±17	
		$-\langle\Delta E_{vib}\rangle$	-156±13		-188±15	
		$-\langle\Delta E_{rot}\rangle$	-27		-26	

*: From Ref. 8.

Table 2 Energy transfer of excited C_6F_6 colliding with ground state C_6F_6（unit：cm^{-1}）

E′	Energy transfer	C_6F_6+ C_6F_6		C_6H_6+ C_6H_6	
		Excited C_6F_6	Ground state C_6F_6	Excited C_6H_6	Ground state C_6H_6
24000	$-\langle\Delta E_{tot}\rangle$	247±46	-216±43		
	$-\langle\Delta E_{vib}\rangle$	314±49	-196±34	680[b]	
	$-\langle\Delta E_{vib}\rangle_{expt}$	736[a]		931[c]	
	$-\langle\Delta E_{rot}\rangle$	-67	-20		
34000	$-\langle\Delta E_{tot}\rangle$	317±33	-286±32		
	$-\langle\Delta E_{vib}\rangle$	404±33	-249±25	930[b]	
	$-\langle\Delta E_{vib}\rangle_{expt}$	1043[a]			
	$-\langle\Delta E_{rot}\rangle$	-87	-37		
40200	$-\langle\Delta E_{tot}\rangle$	550±66	-475±57		
	$-\langle\Delta E_{vib}\rangle$	645±78	-409±55		
	$-\langle\Delta E_{vib}\rangle_{expt}$	1233[a]			
	$-\langle\Delta E_{rot}\rangle$	-95	-66		
40700	$-\langle\Delta E_{vib}\rangle$			1076[b]	-946[b]

a: from Ref. 4. b: from Ref. 11. c: from Ref. 9.

Collision with ground state C_6F_6

The results of CET between excited C_6F_6 and ground state C_6F_6 are given in **Table 2.** First, the results is consistent with the law which - $\langle \Delta E_{vib} \rangle$ of excited C_6F_6 increases with E′ . Second, C_6F_6 transfers more vibrational energy than C_6H_6 when colliding with almost all of the same bath gas except colliding with itself. Our calculation results show that excited C_6F_6 transfers less energy to ground state C_6F_6 than that of excited C_6H_6 transfers to ground state C_6H_6 at same E′. Experimental studies indicate the same order. Our calculation results show that excited C_6F_6 transfers its vibrational energy mainly to vibrational contributions of ground state C_6F_6, so it is V-V energy transfer, such as energy transfer between excited C_6H_6 and ground state C_6H_6[11]. Excited molecule is the same kind as ground state, so they have completely same vibrational frequencies and V-V resonance energy transfer can take place. This kind of energy transfer takes place so fast that it can accomplish in 10^{-12} seconds. We think V-V resonance energy transfer takes place also mainly on low frequencies of molecules such as C_6F_6 and C_6H_6, but interaction time does not decide how much energy can be transferred again. Ground state molecule could turn up its first vibrational excited state of a low frequency by once collision. So the more big frequencies the more energy transferred. The low frequencies of C_6H_6 are bigger than those of C_6F_6, so excited C_6H_6 transfers more vibrational energy to ground state C_6H_6 than that of between C_6H_6 at same E′ .

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