10646 *J. Phys. Chem. A* **2001,** *105,* 10646−10650

Gateway Modes for Collisional Energy Transfer between Benzene and Ar

V. Bernshtein and I. Oref*

Department of Chemistry, Technion-Israel institute of Technology, Haifa 32000, Israel

Received: June 6, 2001; In Final Form: August 14, 2001

Quasiclassical trajectory calculations were used to explore the mechanism of collisional energy transfer between a benzene molecule and an Ar bath gas. Using single mode excitation, it was found that there are two factors that affect energy transfer: the frequency and the type of molecular motion that is associated with the mode. We find that the lowest frequency, out-of-plane torsion mode, is the gateway mode for energy transfer. When the same frequency is assigned also to the in-plane mode, the out-of-plane mode is still more efficient. Only when the frequencies of the out-of-plane and the in-plane modes are switched, the in-plane mode becomes the gateway mode for energy transfer. Therefore, the lowest the frequency is always the gateway mode, and given two modes of identical frequencies, the molecular motions determine the efficiency of energy transfer. These results agree with quantum calculations by Clary et al. [Clary et al. *Faraday Discuss.* **1995**, *102*, 423]. It is found that translation/rotation is a major channel of energy transfer and that vibration/translation energy transfer is efficiently mediated by rotations.

Introduction

It is well-known that collisional energy transfer (CET) plays a major role in chemical, photochemical, and photophysical processes.[1] Activation and deactivation of molecules are the vehicles through which energy is pumped in and out of molecules enabling them to undergo chemical transformation. What is less known is the detailed mechanism of the energy transfer process, in particular, the contribution of individual vibrational modes in a highly excited molecule to CET. The present work explores the details of CET by using quasiclassical trajectory calculations and compares the results with quantum scattering calculations reported by Clary, Gilbert, Bernshtein, and Oref[2] (CGBO).

Previous investigations using quasiclassical trajectory calculations have shed light on some aspects of the mechanism of CET.[3] It was found that for collisions of excited toluene with Ar bath, the average collision duration is short ∼600 fs at 500 K and 230 fs at 1000 K.[3c] This precludes, for most collisions, a long-lived collision complex. Because there is a distribution of lifetimes, some collisions are of long duration of several picoseconds. However, the contribution of the latter to the average energy transferred, $\langle \Delta E \rangle$, is negligible.[3c] We also know that the there is no correlation between a collision lifetime and the value of ΔE transferred in a collision. Even though the collision duration is hundreds of femtoseconds, the actual process of CET occurs instantaneously in the final few tens of femtoseconds of the collision when the bath atom or molecule climbs the repulsive wall of the intermolecular potential.[3c]

It is also known that rotational energy plays a major role in CET.[4] The vibration-to-translation (V/T) CET is greatly enhanced by the mediation of rotations via vibration/rotation coupling that enhances the CET (V/R/T) process. Collisions of a highly excited nonrotating benzene molecule with an Ar bath show less energy transfer than a rotating molecule.[4] It also appears that in extremely energetic collisions (supercollisions) of an excited benzene molecule with an Ar bath out-of-plane modes (OOP) play a major role in the CET process, whereas the other molecular modes play a lesser role and hardly take part in the actual CET.[4,5] Despite the great insight that we have on the nature of CET, we really do not know which modes are active in CET of normal collisions, especially of highly excited molecules. Does the OOP mode play a major role in the CET process, and if so, why does it depend specifically on it? Is the low frequency of the OOP vibration the major factor in CET or is it the wide-angle motion of the OOP torsion, which is primarily responsible for its energy transfer efficiency compared with other types of modes in the benzene molecule?

CGBO[2] have studied CET in benzene/He collisions by vibrational close-coupling, infinite-order sudden quantum scattering computations. They find that in an excited molecule, only the lowest frequency modes, the 398 cm^{-1} OOP and the 606 cm^{-1} in-plane (IP), gave CET cross-sections of appreciable magnitude. The C−H stretching vibrations do not contribute appreciably to the CET. To distinguish between the effect of magnitude and the effect of geometry of the vibrations on CET, the IP motion was assigned the same frequency as the OOP vibration. The OOP motion was found to be more effective than the IP motion over all ranges of ΔE although both modes have the same frequencies. Thus, CGBO's study shows that geometry affects the efficiency of CET. Similar results were obtained for the *p*-difluorobenzene/He system.[6] The quantum scattering results also agree with experimental and trajectory calculations on supercollisions.[4,7−9]

Mentioned in CGBO's paper is the desirability of performing an exact comparison between quantum and quasiclassical trajectory calculations by performing mode specific excitation of OOP and IP motions in quasiclassical trajectory calculations. With this motivation in mind, we have developed in the past few years computational capabilities that enable us to perform quasiclassical trajectory calculations under single mode excitation and frequency switching. In the work described below, we excite a single OOP, IP, or C−H stretching mode in a benzene molecule and follow the CET to an Ar bath atom. To distinguish

---

* To whom correspondence should be addressed. Fax: +972 4829 3643. E-mail: chroref@aluf.technion.ac.il.

10.1021/jp012175g CCC: $20.00

between geometric effects and frequency effects on CET, we have assigned to the IP mode the same frequency as the OOP mode and also have switched the IP frequency with the OOP frequency and have calculated the effect of the changes on the values of $\langle \Delta E \rangle$.

Theory

The numerical methods used in the present work are reported in refs 3c and 10. The equations of motion are integrated by using a modified public domain program Venus.[11] The intermolecular potential is pairwise fitted ab initio[12] potential by Bludsky, Spirko, Herouda, and Hobza (BSHH).[12] They have reported ab initio calculations of an Ar−benzene cluster and fitted the results to a potential function which contains pairwise atom−atom interactions. This is called the BSHH potential:

$$V_{ij} = \frac{A_{ij}}{r_{ij}^{\alpha}} - B_{ij}\left(\frac{1}{r_{ij}^{\ 6}} - \frac{C_{ij}}{r_{ij}^{\ 7}}\right); \quad i = 1-6 \tag{1}$$

A, B, C, and α are constants, r is the distance, i indicates a carbon or a hydrogen atom, and j indicates an argon atom.

The intramolecular potential includes all of the normal mode contributions, stretching, bending, wagging, and torsion. The values of the parameters of this potential were obtained from the modified valence force field calculations by Draeger[13] and are also given in refs 3c and 10. Normal-mode analysis gave good agreement with experimental values. The OOP and IP frequencies were found to be 400 cm^{-1} (exp. 398) and 617 cm^{-1} (exp. 606). The initial translational and rotational energies were chosen from the appropriate thermal energy distributions or assigned specific values. The initial impact parameter was chosen randomly from values between 0 and its maximum value b_{m}. The value of the maximum impact parameter b_{m} was determined separately.[3,10] A value of 0.9 nm was used in the present calculations. The initial internal energy was either the average thermal energy or an assigned value. In thermal systems, the energy was distributed statistically among all of the normal modes of the molecule. In mode specific excitation, the energy was placed in the single mode of choice. In the frequency shuffling, the 617 cm^{-1} frequency of the IP mode was assigned the same frequency as the OOP mode. In another set of calculations, frequencies were exchanged. The frequency of the IP mode was changed to the 408 cm^{-1} frequency of the OOP mode, and the OOP mode was assigned the frequency of the IP mode. A total of 10 000 trajectories were used for each set of initial conditions. The large number of trajectories was chosen to provide good statistical sampling in the binning process.

Results and Discussion

The first part of the present study compares quantum scattering and quasiclassical calculations at low levels of excitation, dictated by computational constrains on the quantum system. In the second part, CET quantities at (experimental) high levels of excitation are explored. In analyzing CET results it is important to take cognizance of the various energy transfer channels that are operational in a binary collision: (a) up collisions where translation to rotation (T/R) and/or translation to vibration (T/V) take place and (b) down collisions where V/T, V/R, R/T, or V/R/T are operational. The average overall energy transferred in a collision $\langle \Delta E \rangle_{\mathrm{all}}$ does not represent the detailed processes that take place during the CET. For example, there can be a large exchange of energy between vibration and rotation with a minimal net energy loss to translation. In this case, $\langle \Delta E \rangle_{\mathrm{all}}$ is small, whereas the internal energy loss is large with subsequent effects on chemical and photophysical processes. We have, therefore, in the present study, calculated the values of $\langle \Delta E \rangle$ for all the individual channels of CET. That is to say, in addition to evaluating $\langle \Delta E \rangle_{\mathrm{d}}$, $\langle \Delta E \rangle_{\mathrm{u}}$, and $\langle \Delta E \rangle_{\mathrm{all}}$, we have evaluated $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{d}}$, $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{u}}$, and $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{all}}$ as well as $\langle \Delta E_{\mathrm{r}} \rangle_{\mathrm{d}}$, $\langle \Delta E_{\mathrm{r}} \rangle_{\mathrm{u}}$, and $\langle \Delta E_{\mathrm{r}} \rangle_{\mathrm{all}}$. In this notation, d indicates down and u indicates up collisions and v and r indicate vibrational and rotational energy, respectively. The subscript "all" indicates the net energy transfer emanating from all up and down collisions. We have chosen to focus extra attention on the values of $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{d}}$ because this quantity best describes a "deactivating collision", a collision that removes internal vibrational energy and, therefore, directly affects chemical reactivity and photophysical activity. Of course, overall rotations, in addition to facilitating vibrational/rotational coupling, also affect reactivity through centrifugal effects but these might be regarded as second-order effects. Internal rotations are lumped together with internal energy quantities.

To determine which frequencies serve as gateway frequencies for energy transfer we have used single mode excitation (SME). The following SMEs were used. (a) Energy was placed in the 400 cm^{-1} OOP and in the 617 cm^{-1} IP modes of a nonrotating molecule. Values of the relative translational energy were chosen to match identical conditions in quantum scattering calculations. (b) The same conditions as in (a) but the relative translational energy was chosen from a thermal distribution. (c) For photoexcitation systems, the photon energies were distributed statistically among the normal modes and converted into vibrational temperatures,[14] and the average internal energy for each mode was calculated.[14] Then, in each run, a given mode was excited by placing in it the appropriate average internal energy, including the degeneracy.

The first set of initial conditions was designed in order to compare the quantum scattering calculations of CGBO with our quasiclassical computations. The results are presented in Table 1. First, varying amounts of energy were placed only in the 400 cm^{-1} doubly degenerate E_{2g} lowest-lying OOP vibration. Next, the 617 cm^{-1}, doubly degenerate, E_{2u} IP vibration was excited. The translational energy was 807 cm^{-1} (0.1 eV), identical with CGBO's value, and the rotational temperature was 0 K. As can be seen, at all internal energies, the OOP mode is more efficient than the IP mode as far as $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{d}}$ is concerned, whereas the nature of the excited mode hardly affects the value of $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{u}}$. This is to be expected because up collisions have many CET channels available for energy transfer. There are no restrictions on VR/T coupling, and rotations are much more efficient in CET than pure vibrations. In addition, the rest of the molecular modes were examined separately at the same excitation energies as the OOP and the IP modes. No significant contributions of those modes to the CET were found.

To check whether the low frequency of the OOP motion is responsible for the efficient energy transfer or it is the dynamic nature of the OOP frequency, we have followed CGBO and changed the IP frequency to be the same as the OOP frequency. (The change in the force constants of the IP modes reduced also the B_{2u} ring deformation modes from 1026 to 643 cm^{-1}.) Although the IP frequency is identical to the OOP frequency, the latter mode proved to be the gateway mode for the vibrational down collisions. That is to say, $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{d}}$ proved to be the largest for the OOP frequency at all assigned initial energies. These results agree with CGBO's, who found that the OOP

TABLE 1: Collisional Energy Transfer between Ar and Single-Mode Excited Benzene[a]

excited modes	E_{v}	$\langle \Delta E\rangle_{\mathrm{all}}$	$-\langle \Delta E\rangle_{\mathrm{d}}$	$\langle \Delta E\rangle_{\mathrm{u}}$	$\langle \Delta E_{\mathrm{v}}\rangle_{\mathrm{all}}$	$-\langle \Delta E_{\mathrm{v}}\rangle_{\mathrm{d}}$	$\langle \Delta E_{\mathrm{v}}\rangle_{\mathrm{u}}$	$\langle \Delta E_{\mathrm{r}}\rangle_{\mathrm{all}}$	$\langle \Delta E_{\mathrm{r}}\rangle_{\mathrm{u}}$
Part 1: The Excited Modes Were the E_{2u} 400 cm^{-1} OOP or the E_{2g} 617 cm^{-1} IP. The Translational Energy is 800 cm^{-1} (0.1 eV)									
OOP	3500	**239**	46	242	**34**	37	59	**205**	205
IP	3500	**213**		213	**34**	8	47	**179**	179
OOP	7000	**208**	44	212	**26**	43	57	**182**	182
IP	7000	**195**		196	**34**	8	50	**161**	161
OOP	12280	**183**	40	190	**17**	55	60	**166**	166
IP	12280	**186**		189	**34**	10	54	**152**	152
Part 2: OOP and IP as above. The Translational Energy is 420 cm^{-1}									
OOP	3500	**125**	19	127	**28**	13	39	**97**	97
IP	3500	**118**		118	**27**	5	33	**91**	91
OOP	7000	**115**	25	118	**25**	17	40	**90**	90
IP	7000	**111**		111	**26**	5	34	**85**	85
OOP	12280	**107**	36	112	**22**	22	43	**85**	85
IP	12280	**107**		107	**26**	6	37	**81**	81
Part 3: The IP Is the Same as the OOP Frequency. The Translational Energy is 800 cm^{-1} (0.1 eV)									
OOP	3500	**240**	33	243	**36**	35	61	**204**	204
IP	3500	**210**	22	213	**33**	18	52	**178**	178
OOP	7000	**208**	36	213	**25**	47	64	**182**	182
IP	7000	**191**	16	195	**29**	23	54	**162**	162
OOP	12280	**189**	31	197	**19**	64	70	**170**	170
IP	12280	**179**	17	187	**31**	29	58	**148**	148
Part 4: The IP Is the Same as the OOP Frequency. The Translational Energy is 420 cm^{-1}									
OOP	3500	**128**	25	130	**29**	14	40	**98**	98
IP	3500	**115**	17	116	**27**	7	36	**88**	88
OOP	7000	**117**	37	121	**25**	21	43	**91**	91
IP	7000	**108**	16	110	**25**	12	38	**83**	83
OOP	12280	**109**	34	116	**22**	29	49	**87**	87
IP	12280	**102**	14	107	**25**	13	40	**76**	76

[a] The rotational temperature is 0 K. Each run included 10 000 trajectories. Energies are in cm^{-1}. $\langle \Delta E_{\mathrm{r}}\rangle_{\mathrm{d}} = 0$.

TABLE 2: Collisional Energy Transfer between Ar and Single-Mode Excited Benzene[a]

excited modes	E_{v}	$\langle \Delta E\rangle_{\mathrm{all}}$	$-\langle \Delta E\rangle_{\mathrm{d}}$	$\langle \Delta E\rangle_{\mathrm{u}}$	$\langle \Delta E_{\mathrm{v}}\rangle_{\mathrm{all}}$	$-\langle \Delta E_{\mathrm{v}}\rangle_{\mathrm{d}}$	$\langle \Delta E_{\mathrm{v}}\rangle_{\mathrm{u}}$	$\langle \Delta E_{\mathrm{r}}\rangle_{\mathrm{all}}$	$\langle \Delta E_{\mathrm{r}}\rangle_{\mathrm{u}}$
Part 1: The Excited Modes Were the E_{2u} 400 cm^{-1} OOP or the E_{2g} 617 cm^{-1} IP									
OOP	3500	**155**	20	158	**27**	23	43	**128**	128
IP	3500	**147**		147	**29**	6	36	**118**	118
OOP	7000	**144**	31	148	**23**	28	45	**122**	122
IP	7000	**138**		138	**28**	7	38	**110**	110
OOP	12280	**129**	41	135	**18**	40	48	**111**	111
IP	12280	**134**	1	136	**30**	8	43	**105**	105
Part 2: Both OOP and IP Have the Same 400 cm^{-1} Frequency									
OOP	3500	**159**	23	162	**29**	24	44	**130**	130
IP	3500	**141**	28	144	**25**	16	38	**116**	116
OOP	7000	**144**	30	149	**23**	34	47	**121**	121
IP	7000	**132**	17	135	**24**	19	40	**108**	108
OOP	12280	**135**	30	142	**20**	42	51	**115**	115
IP	12280	**126**	151	131	**26**	21	43	**100**	100
Part 3: The OOP and IP Frequencies Were Swapped, OOP is 617 and IP 400 cm^{-1}									
OOP	3500	**169**		169	**35**	4	40	**134**	134
IP	3500	**143**	24	146	**28**	16	41	**115**	115
OOP	7000	**162**		163	**38**	7	45	**125**	125
IP	7000	**130**	29	134	**23**	24	40	**107**	107
OOP	12280	**141**	22	144	**33**	15	46	**108**	108
IP	12280	**123**	33	132	**22**	24	47	**99**	99

[a] The rotational temperature is 0 K and the translational temperature is 300 K (420 cm^{-1}). Each run included 10 000−30 000 trajectories. Energies are in cm^{-1}. $\langle \Delta E_{\mathrm{r}}\rangle_{\mathrm{d}} = 0$.

mode is the most efficient even when the OOP and the IP modes have the same frequencies.

To check whether the results depend on the translational energy, we have performed identical calculations with initial relative translational energy of 420 cm^{-1} (0.052 eV), which is the average relative translational energy at 300 K. The results in Table 1 show that the conclusions reached before are independent of the translational energy. The same conclusions were obtained from a similar set of experiments, reported in Table 2, where the single average value of the translational energy was replaced by a thermal distribution at 300 K. This set of calculations consistently gave larger absolute values for $\langle \Delta E\rangle$ than the single average value of the translational energy. This is to be expected because the high-energy tail of the distribution contributes more to the values of $\langle \Delta E\rangle$ than the single average value.

In addition to repeating the calculations reported above with a thermal distribution of translational energy instead of a single value, we have calculated the values of $\langle \Delta E\rangle$ for a case where the IP and OOP frequencies were swapped and the IP became the lowest frequency mode. Here, the IP mode became the gateway frequency for energy transfer. The OOP mode is active

TABLE 3: Energy Transfer Quantities as a Function of Energy in a Single Mode[a]

excited modes	E_v	$\langle\Delta E\rangle_{all}$	$-\langle\Delta E\rangle_d$	$\langle\Delta E\rangle_u$	$\langle\Delta E_v\rangle_{all}$	$-\langle\Delta E_v\rangle_d$	$\langle\Delta E_v\rangle_u$	$\langle\Delta E_r\rangle_{all}$	$-\langle\Delta E_r\rangle_d$	$\langle\Delta E_r\rangle_u$
out of plane Torsions $\mathbf{E_{2u}}$ 400	2175 × 2	**18**	185	173	**8**	59	77	**9**	180	165
in plane $\mathbf{E_{2g}}$ Ring deform 617	2070 × 2	**21**	164	165	**24**	40	68	**−3**	171	157
ring deform $\mathbf{B_{2g}}$ 657	2070	**20**	187	185	**21**	33	66	**−1**	188	169
CH bend $\mathbf{A_{2u}}$ 680	2035	**22**	184	180	**24**	35	60	**−1**	185	163
CH bend $\mathbf{E_{1g}}$ 832	1965 × 2	**25**	183	183	**25**	32	62	**0**	185	169
ring stretch $\mathbf{A_{1g}}$ 926	1930	**24**	179	179	**24**	34	63	**0**	182	164
CH bend $\mathbf{E_{1u}}$ 991	1910 × 2	**24**	187	185	**27**	34	64	**−2**	187	172
CH bend $\mathbf{E_{2u}}$ 1015	1895 × 2	**25**	186	184	**26**	34	64	**−1**	186	171
CH bend $\mathbf{B_{2g}}$ 1070	1860	**22**	184	185	**23**	36	59	**−1**	187	169
ring deform $\mathbf{B_{2u}}$ 1026	1860	**20**	190	186	**18**	36	59	**2**	192	170
CH bend $\mathbf{E_{2g}}$ 1134	1860 × 2	**20**	184	181	**20**	31	60	**1**	183	168
CH bend $\mathbf{B_{2u}}$ 1173	1825	**20**	188	186	**21**	34	59	**−1**	189	170
CH bend $\mathbf{A_{2g}}$ 1375	1754	**22**	189	185	**22**	35	61	**−1**	190	168
ring str+def $\mathbf{E_{2u}}$ 1530	1684 × 2	**24**	196	188	**25**	34	61	**0**	193	176
ring stretch $\mathbf{E_{2g}}$ 1739	1596 × 2	**25**	195	188	**25**	34	62	**0**	194	174
ring stretch $\mathbf{B_{2u}}$ 1749	1614	**23**	196	193	**24**	38	61	**−1**	197	176
CH stretch $\mathbf{A_{1g}}$, $\mathbf{E_{2u}}$, $\mathbf{E_{2g}}$, $\mathbf{B_{1u}}$ 3060	1164 × 6	**25**	183	182	**22**	35	57	**3**	183	169

[a] The internal energy of 52 270 cm^{-1} is distributed statistically among the various modes, and each mode is excited in a separate run. The rotational and translational temperatures are 300 K, and the total number of trajectories in each run is 11 000. Energies and normal mode frequencies are in cm^{-1} and time is in picoseconds. All degenerate modes (indicated by x) were excited simultaneously.

TABLE 4: Energy Transfer Quantities for C−H Stretching Mode as a Function of the Rotational and Translational Temperatures in K[a]

T_r	T_t	$\langle\Delta E\rangle_{all}$	$-\langle\Delta E\rangle_d$	$\langle\Delta E\rangle_u$	$\langle\Delta E_v\rangle_{all}$	$-\langle\Delta E_v\rangle_d$	$\langle\Delta E_v\rangle_u$	$\langle\Delta E_r\rangle_{all}$	$-\langle\Delta E_r\rangle_d$	$\langle\Delta E_r\rangle_u$
300	300	**25**	183	182	**22**	35	57	**3**	183	169
400	300	**−18**	232	181	**22**	44	64	**−39**	233	170
500	300	**−59**	278	180	**22**	52	72	**−82**	284	169
600	300	**−95**	325	178	**24**	58	80	**−119**	327	174
300	300	**25**	183	182	**22**	35	57	**3**	183	169
300	400	**58**	184	226	**25**	34	63	**33**	183	207
300	500	**87**	184	264	**32**	34	71	**55**	187	237
300	600	**125**	180	301	**36**	34	73	**89**	186	272
300	300	**25**	183	182	**22**	35	57	**3**	183	169
400	400	**17**	236	217	**26**	43	68	**−8**	235	202
500	500	**11**	283	260	**29**	54	78	**−17**	285	245
600	600	**−1**	325	295	**35**	61	91	**−36**	342	276

[a] The internal energy of 52 270 cm^{-1} is assumed to be distributed statistically among the various modes, but only the C−H energy, 1164 cm^{-1}, is placed in each of the six C−H stretching modes. The total number of trajectories in each run is 11 000. Energies and normal mode frequencies are in cm^{-1}.

as well in the CET but does not contribute as much as does the lower frequency IP mode. This is in contrast to the case where the OOP and the IP modes are assigned their normal frequencies; the IP mode is inactive and hardly contributes to the CET process. It can be concluded therefore that there are two factors that dominate CET. The most important is the frequency: the lower the better. The second is the nature of the mode. OOP motions are more effective than IP motions. There is good agreement between our quasiclassical results and the quantum scattering results of CGBO's even though the latter were performed on the He/benzene system, whereas the present results are for Ar/benzene collisions. However, we do expect the trends reported above to be valid for all inert gas/benzene collisions. Our results also agree with those of Lendvay,[15] who found that the gateway mode in linear CS_2 is the lowest-frequency bending mode. The findings that the low-frequency mode is the gateway for CET support the sequential direct encounter model of Dashevskaya et al.[16,17] which assumes that the low-frequency mode is the gateway mode for CET.

As mentioned before, rotations play a major role in CET.[4] Most of the CET occurs via a T/R mechanism where the translational energy goes into rotation. The global effect of rotation on CET masks the mechanism of direct V/T transfer. This is confirmed in the present very detailed study of SME and can be concluded from the results in Table 1, where the values of $\langle\Delta E_r\rangle_{all}$ are a factor of ∼3−5 larger than the values of $\langle\Delta E_v\rangle_d$. Therefore, rotations are the major contributors to the values of $\langle\Delta E\rangle_{all}$ in all specific modes excitation energies. This conclusion is supported by the work of Koifman et al.[18] and Rosenblum et al.,[19] who found that in SO_2 rare gas collisions and rotations are the major energy transferring mode.

The next set of computations were designed to explore CET experiments by Barker et al.[20−22] where a benzene molecule is excited by a photon and is deactivated by collisions with Ar. In our calculations, a 52 270 cm^{-1} photon energy is allowed to undergo statistical redistribution and the average energy in each mode is computed and allocated to each mode.[14] To resemble the experimental conditions, the rotational and translational energies were chosen from their thermal distributions at 300 K. In a series of runs, each mode of the benzene molecule was excited separately and was allocated the proportional amount of energy according to the vibrational temperature of the molecule at the 52270 cm^{-1} excitation energy. The results are given in Table 3, and they clearly indicate that the gateway mode is the lowest frequency OOP mode with $\langle\Delta E_v\rangle_d$ almost twice as large as for the other modes. The second lowest frequency IP mode is more efficient than the other modes but not as efficient as the OOP mode. The OOP mode does not, of course, affect rotational CET; therefore, $\langle\Delta E_r\rangle_d$ and $\langle\Delta E_r\rangle_u$ are approximately the same for all of the modes. Not only are these two quantities the same for all modes, they are almost equal to each other, and therefore, the value of $\langle\Delta E_r\rangle_{all}$ is approximately zero as expected from a thermalized system. The contributions to $\langle\Delta E\rangle_{all}$ come only from V/T processes, in a stark contrast to the cold molecule case, which is represented in Table 1, where the major contribution to $\langle \Delta E \rangle_{\mathrm{all}}$ comes from rotations.

The relative contributions of rotations and translations to CET from the C−H stretching modes are reported in Table 3. Some of the calculations model the CET experiments of Barker et al.[20−22] which involve photoexcitation followed by infrared emission from a C−H stretching mode. In the first set of results, the translational energy is kept constant at 300 K and the rotational temperature varies from 300 to 600 K. As the rotational temperature increases, the absolute values of $\langle \Delta E_{\mathrm{r}} \rangle_{\mathrm{d}}$ increase and so do the values of $\langle \Delta E_{\mathrm{r}} \rangle_{\mathrm{all}}$. Down collision via R/T CET prevail, as can be expected in a system where the rotations are hotter than the translations, and the rotational contribution to $\langle \Delta E \rangle_{\mathrm{all}}$ increases as the system moves farther from equilibrium. Both $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{d}}$ and $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{u}}$ increase with rotational temperature, rendering $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{all}}$ constant. In a second set of initial conditions, the rotations are kept constant at 300 K and the translations vary in the range 300−600 K; up collisions prevail as rotational heating occurs in the energy exchange process. It is important to note that $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{d}}$ does not change at all. That is to say, vibrational CET of the C−H stretching mode is not affected by translations. This is clearly not the case for variable rotational temperature discussed before where $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{d}}$ changes with the rotational temperature. Increasing the temperature of a thermal system where the rotational and translational temperatures are identical increases the values of all of the CET quantities. Vibrational and rotational CET are both affected mainly by rotations that serve as an efficient CET moderator.

As a general check of our computations, we have compared our results for $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{d}}$ with experimental results of Barker et al.[20−22] for CET between photoexcited benzene and Ar at 300 K. Our trajectory results yield $\langle \Delta E_{\mathrm{v}} \rangle_{\mathrm{d}} = 35\ \mathrm{cm}^{-1}$ as compared with the experimental value of $35.2\ \mathrm{cm}^{-1}$ evaluated from a best fit formula reported in ref 22. This agreement is fortuitous but clearly indicate the reliability of our computations.

In summary, using single mode excitation of the various modes of the benzene molecule, we have found that the gateway mode for collisional energy transfer is the lowest frequency OOP mode. In addition to the low frequency, but to a lesser extent, the geometry of the mode plays a role in the efficiency of the energy transfer. The OOP molecular motions are more effective than the IP mode or any other molecular mode. When both OOP and IP modes have the same frequency, the OOP mode is more efficient than the IP mode. However, when the frequencies of the two mode are switched and the IP mode is the lowest frequency mode, it becomes the gateway mode for energy transfer. Rotations play a crucial role in the energy transfer process. Most of the energy exchange is between rotation and translations. Vibrational energy loss is often mediated by rotation. There is good agreement between the quantum scattering calculations of Clary et al.[2] and the present quasiclassical trajectory calculations, which also reproduce the experimental results of Barker et al.[20−22]

Acknowledgment. This work is supported by the Technion V. P. R. Fund, by E. and M. Mendelson Research Fund, by the fund for promotion of research at the Technion, and by the Ministry of Science and the Arts.

References and Notes

(1) Oref, I.; Tardy, D. C. *Chem. Rev.* **1990**, *90*, 1407.

(2) Clary, D. C.; Gilbert, R. G.; Bernshtein, V.; Oref, I. *Faraday Discuss.* **1995**, *102*, 423.

(3) (a) Miller, J. A.; Brown, N. J. *J. Phys. Chem.* **1982**, *86*, 772. (b) Brown, N. J.; Miller, J. A. *J. Chem. Phys.* **1984**, *80*, 5568. (c) Bernshtein, V.; Oref, I. *J. Phys. Chem.* **1995**, *99*, 4531.

(4) Bernshtein, V.; Lim, K. F.; Oref, I. *J. Chem. Phys.* **1997**, *106*, 7080.

(5) Bernshtein, V.; Oref, I. *ACS Symp. Ser.* **1997**, *678*, 251.

(6) Clary, D. C. *J. Chem. Phys.* **1987**, *86*, 802.

(7) Pashutski, A.; Oref, I. *J. Phys. Chem.* **1988**, *92*, 178.

(8) Hassoon, S.; Oref, I.; Steel, C. *J. Chem. Phys.* **1988**, *89*, 1743.

(9) Morgulis, J. M.; Sapers, S. S.; Steel, C.; Oref, I. *J. Chem. Phys.* **1989**, *90*, 923.

(10) Bernshtein, V.; Oref, I. *Chem. Phys. Lett.* **1994**, *233*, 173.

(11) Venus, Quantum Chemistry Program Exchange; Hase, W. L.; Duchovic, R. J.; Hu, X.; Komornicki, A.; Lim, K. F.; Lu, D.-H.; Peslherbe, G. H.; Swamy, K. N.; Vande-Linde, S. R.; Varandas, A.; Wang, H.; Rolf, R. J. *Quant. Chem. Program Exchange Bull.* **1996**, *16* (4), 43 [QCPE Program 671].

(12) Bludsky, O.; Spirko, V.; Hrouda, V.; Hobza, P. *Chem. Phys. Lett.* **1992**, *196*, 410.

(13) Draeger, J. A. *Spectrochim. Acta* **1985**, *41A*, 607.

(14) Park, J.; Bersohn, R.; Oref, I. *J. Chem. Phys.* **1990**, *93*, 5700.

(15) Lendvay, G. *J. Phys. Chem. A* **1997**, *101*, 9217.

(16) Dashevskaya, E. I.; Nikitin, E. E.; Oref, I. *J. Phys. Chem.* **1993**, *97*, 9397.

(17) Dashevskaya, E. I.; Nikitin, E. E.; Oref, I. *J. Phys. Chem.* **1995**, *99*, 10797.

(18) Koifman, I.; Dashevskaya, E. I.; Nikitin, E. E.; Troe, J. *J. Phys. Chem.* **1995**, *99*, 15348.

(19) Rosenblum, I.; Dashevskaya, E. I.; Nikitin, E. E.; Oref, I. *Mol. Eng.* **1997**, *7*, 169.

(20) Yerram, M. L.; Brenner, J. D.; King, K. D.; Barker, J. R. *J. Phys. Chem.* **1990**, *94*, 6341.

(21) Brenner, J. D.; Erinjeri, J. P.; Barker, J. R. *Chem. Phys.* **1993**, *175*, 99.

(22) Barker, J. R.; Toselli, B. M. *Int. Rev. Phys. Chem.* **1993**, *12*, 305.