J. Phys. Chem. A **2003,** *107,* 10507−10513 **10507**

Relaxation of the 6^1 Vibrational Level in $^1B_{2u}$ Benzene by Polyatomic Colliders at Ultralow Temperatures[†]

Eric R. Waclawik and Warren D. Lawrance*

School of Chemistry, Physics and Earth Sciences, Flinders University, GPO Box 2100,
Adelaide South Australia 5001, Australia

Received: January 16, 2003; In Final Form: September 11, 2003

Vibrational energy transfer from the 6^1 level of S_1 ($^1B_{2u}$) benzene has been studied at low collision energies in supersonic free jet expansions with 11 polyatomic collision partners. Each of the collision partners has available low lying vibrational levels so that relaxation can proceed via transfer of vibration in benzene to vibration in the collision partner (V → V transfer). Transfer to the 0^0 level of benzene is significant with each of these partners. From (a) comparisons with the behavior of the monatomic, diatomic, and small polyatomic partners studied previously and (b) previous results at room temperature [C. S. Parmenter, C. S.; Tang, K. Y. *Chem. Phys.* **1978**, *27*, 127], it is deduced that V → V transfer is responsible for the dominance of the $6^1 \rightarrow 0^0$ pathway. It is observed that the branching ratios for transfer to 0^0 are consistently largest for straight chain partners. The rotational contours of collisionally populated levels are fairly broad, revealing that significant rotational excitation accompanies vibrational relaxation. Boltzmann distribution fits to the rotational contours for 0^0 give temperatures that are on average slightly lower than those found for small polyatomics. The observation that a reasonable amount of energy is transferred into benzene rotation suggests that it is the low-frequency modes of the collision partner that are excited. Resonant or near resonant transfer appears to be inefficient. V → V and V → R transfer both appear to be operating in relaxation of 6^1 benzene yet are absent in relaxation from the related case of 6^1 *p*-difluorobenzene [Mudjijono; Lawrance, W. D. *J. Chem. Phys.* **1996**, *105*, 9874]. It is suggested that this difference arises because of a reduced efficiency for V → T transfer in the benzene case due to the 112 cm^{-1} higher frequency of ν_6 in this molecule.

1. Introduction

The relaxation of nonequilibrium gas-phase systems occurs via collisions that can alter the vibrational energy of the constituent molecules. State-to-state studies of vibrational energy transfer (VET) in sparse regions of the vibrational manifold in large polyatomics provide insight into the vibrational changes favored in collisions.[1−4] Investigations at low temperatures, such as occur in a supersonic free jet expansion, are potentially more sensitive to the details of how vibrational motion is altered in collisions than are room temperature experiments. Room temperature experiments tend to reveal the modes most easily excited in a collision because excitation of the lowest frequency mode is the usual relaxation pathway at room temperature.[1−6] In contrast, this relaxation pathway is removed at low temperatures, and experiments probe how easily one type of motion is either reduced in amplitude ($\Delta v = v_{\text{final}} - v_{\text{initial}} = -1, -2,$ etc.) or converted into a different type of motion (e.g., $\Delta v_{\text{initial mode}} = -1$; $\Delta v_{\text{final mode}} = +1$). Such changes are fundamental to equilibration of nonequilibrium systems because, although the first step in relaxing a system with excess energy typically involves the addition of a low-frequency mode,[1−6] this is intermediate to steps involving loss of energy, which in general requires conversion to another, lower frequency motion.

How the relaxation pathways alter with the collision partner has been the subject of comparatively few studies (a table summarizing previous studies up to 1995 is given in ref 7). In two previous papers we have investigated the effect of the collision partner's translational[7] and rotational[8] degrees of freedom on the state-to-state preferences (branching ratios) for transfer from the 6^1 level of benzene at low temperatures in a supersonic free jet expansion. When the transfer of vibrational energy in the target molecule is accompanied by a simultaneous change of vibrational energy within the collision partner, the process is called V → V transfer. The experiments described in this paper probe V → V transfer from 6^1 benzene in low energy collisions in a supersonic free jet expansion, utilizing the foundation provided by our earlier V → T and V → R,T partner studies. (V → R,T indicates transfer from vibration in benzene to rotation and translation in the collision partner, and analogously for V → T transfer.) VET branching ratios are measured with collision partners that possess low-frequency vibrational modes and can therefore accept energy from 6^1 benzene as vibrational motion.

Very few state-to-state studies of vibrational relaxation within large polyatomic molecules have investigated collisions with polyatomic partners in which it is possible to excite vibrations within the collision partner. In one of the most explicit studies, Parmenter's group probed near resonant transfer from ν_6' in S_1 benzene to the bending mode of OCS at room temperature, finding that the $6^1 \rightarrow 0^0$ transfer is substantially enhanced for this partner relative to comparable partners such as CO_2.[9] Subsequently, Tang and Parmenter studied VET from 11 initial levels of S_1 benzene with isopentane and CO as collision partners and concluded that most of the transfer from low S_1 energies involves excitation of vibrational energy within isopentane.[10] There are only two studies that have probed for V → V transfer with a wide range of collision partners, and these

---

[†] Part of the special issue "Charles S. Parmenter Festschrift".

* To whom correspondence should be addressed. Fax: 61-8-8201 2905. E-mail: warren.lawrance@flinders.edu.au.

10.1021/jp030067j CCC: $25.00 © 2003 American Chemical Society
Published on Web 10/18/2003

TABLE 1: Polyatomic Collision Partners Employed in This Study, with the Number of Vibrational Modes Lower in Energy than the Benzene 6^1 Frequency of 522 cm^{-1}

collision partner	formula	mol wt (amu)	no. of fundamental modes below 522 cm^{-1} [a]
dichloromethane	CH_2Cl_2	50.5	1
ethane	C_2H_6	30	1
propane	C_3H_8	44	3
n-butane	n-C_4H_{10}	58	5
isobutane	i-C_4H_{10}	58	<5[b]
cyclopentane	c-C_5H_{10}	70	1
diethyl ether	$(C_2H_5)_2O$	74	7
n-pentane	n-C_5H_{12}	72	7
isopentane	i-C_5H_{12}	72	<7[b]
neopentane	$C(CH_3)_4$	72	<7[b]
n-hexane	n-C_6H_{14}	86	9

[a] The references to the vibrational frequencies are as follows: dichloromethane,[13] ethane,[13] propane,[14] *n*-butane,[14] isobutane,[15] cyclopentane,[16] diethyl ether,[17] *n*-pentane,[18] isopentane,[15] neopentane,[15] *n*-hexane.[18] [b] The uncertainty arises because of the differences in frequencies for different conformers.

are the pioneering room temperature study of benzene by Parmenter and Tang[11] and a low temperature, supersonic free jet expansion study of *p*-difluorobenzene (*p*-DFB) by our group.[12] Parmenter and Tang found V → V transfer to be efficient and to contribute to relaxation from the 6^1 level in benzene which, as we have noted, is the conclusion also reached in Parmenter's later studies of VET in benzene.[9,10] Interestingly, our study found no evidence for V → V transfer in *p*-DFB. Clear differences between the studies are the temperature at which they have been undertaken and the frequency of ν_6 in these molecules (410 cm^{-1} in *p*-DFB vs 522 cm^{-1} in benzene). Will V → V transfer continue to be sufficiently efficient that it competes with V → T and V → R transfer in benzene at ultralow temperatures and, if it does, why is V → V transfer efficient in benzene but not in *p*-DFB. This study explores these issues?

The polyatomic collision partners used in this study are shown in Table 1. They all possess at least one vibrational level lower in energy than 522 cm^{-1}, the 6^1 benzene vibrational energy. Importantly, they include both long chain partners of the type used in Parmenter and Tang's study and the smaller polyatomics used by Mudjijono and Lawrance. The long chain polyatomic colliders have a number of fundamental, combination, and overtone vibrations that could be excited in collisions with 6^1 benzene. The presence of a number of low-frequency vibrational modes and conformations means that the long chain partners will have a greater number of possible channels by which V → V exchange can be accomplished during a collision with benzene than shorter chain length partners. Ethane, cyclopentane, and dichloromethane are a particularly interesting trio for comparison. Each possesses a single vibrational mode with frequency less than the benzene 6^1 frequency, and the frequency of this mode is similar in these three molecules (275,[13] 283,[16] and 283 cm^{-1},[13] respectively). Thus the energetics relevant to V → V transfer are virtually identical in these three collision partners.

It is important to note that the experiments probe nonresonant V−V transfer. The transfer is of vibrational energy in one molecule to vibrational energy in another where there is, in general, a significant energy separation between the participating states.

2. Experimental Details

The apparatus and techniques used to measure vibrational energy transfer have been presented in the first paper in this series.[7] The technique involves time-resolved dispersed fluorescence (TRDF) detection following laser excitation of an initial vibrational level in an excited electronic state. Vibrational levels populated via collisions appear in the spectrum as extra bands whose intensities grow with time following the laser pulse. VET is monitored in the collision region of a supersonic free jet expansion. The experiments described here were carried out at X/D = 5. Because the experiment is time resolved, multiple collisions can be observed through changes in the state-to-state branching ratios with time. We find no evidence for multiple collisions affecting our results.

By undertaking the experiments in the collision region of a supersonic free jet expansion, there is substantial cooling of the polyatomic collision partner, provided their concentration in the supersonic free jet expansion is maintained at a low level.[19] We find that the polyatomic colliders are far more efficient at inducing vibrational relaxation in a collision than diatomic or triatomic collision partners. Therefore, only a small partial pressure of the polyatomic gas of interest needs to be incorporated in a gas mixture with helium to produce measurable VET induced by the polyatomic. Because helium is a particularly inefficient relaxer of 6^1 benzene,[7,11,20] the state-to-state branching ratios are not influenced by collisions with the helium carrier gas at the low backing pressures used. This is different from the situation in *p*-DFB,[12] and so one cannot take it for granted that this situation applies in all cases.

The experiments are performed at very low backing pressures (<60 kPa). At these pressures vibrational transfer by He is not detectable in our experiment. The low backing pressure also minimizes van der Waals molecule and cluster formation. van der Waals molecules absorb at a wavelength different from that of the monomer, with the magnitude of the red or blue shift indicating the amount of stabilization or destabilization, respectively, of the S_1 complex compared to S_0.[21] By way of illustration for benzene−polyatomic complexes, benzene−water and benzene−acetylene transitions are shifted 50 [22] and 136 cm^{-1} [23,24] to the blue, respectively, whereas benzene dimer and benzene−*p*-difluorobenzene transitions are shifted 40 [25,26] and 62 cm^{-1} [27] to the red, respectively. For this reason, any van der Waals molecules/clusters present are not excited at the benzene monomer wavelength and hence do not influence the measurements through van der Waals dissociation. (Dissociation of van der Waals complexes could lead to emission from benzene monomer.) However, should a large fraction of the collider be incorporated in clusters, the relaxation observed might be contaminated by relaxation due to collisions with clusters. Mass selected REMPI experiments examining the S_0−S_1 spectroscopy of benzene−*p*-difluorobenzene clusters undertaken in our group reveal negligible van der Waals molecules at these low backing pressures at partial pressures comparable to those used here for the collision partners.[27]

Six of the eleven partners are gases at room temperature (we include isopentane with a boiling point of 300 K in this category). For these partners and *n*-pentane, a gas mixture of the polyatomic in helium was prepared and flowed over a reservoir containing benzene at 0 °C prior to pulsed supersonic expansion. The collision partner was typically 10% in helium. These low seed ratios ensure minimal variation in temperature between the various collision partner experiments. The temperature is calculated to be ∼14−15 K.[19] For the remaining four (liquid) partners the pure liquid was contained in a cooled cell of the same design as the benzene sample holder and connected to the free jet gas line in parallel with the cooled benzene cell. Helium carrier gas was then flowed over the two cells to create the backing gas for the free jet expansion. Check

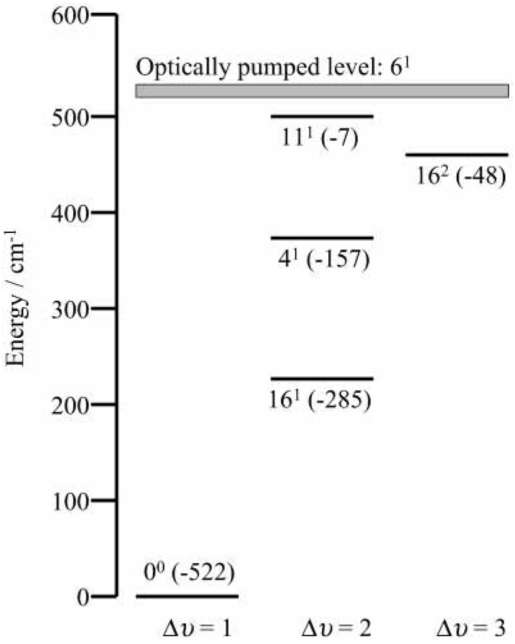

Figure 1. Schematic diagram of the vibrational levels in benzene that can participate in VET from the 6^1 level under supersonic free jet expansion conditions. The energy gap, ΔE, and the vibrational quanta change, $\Delta \upsilon$, involved in transfer to each level is indicated on the diagram.

valves inserted between the different gas lines prevented the benzene and collision partner contaminating each other during a run. Both the collision partner and benzene cells were freeze−pump−thawed three times before a time-resolved dispersed fluorescence (TRDF) spectrum was collected. Sample cell bath temperatures were maintained at constant settings to provide a constant seed ratio. Although this method of sample preparation provides less precise control of the partial pressure of the collider, the spectra indicate a similar amount of VET is occurring for the liquid and gaseous samples, suggesting that the seed ratios are similar.

The state-to-state rate constants are second-order and to determine them the absolute concentration of the partner at the X/D value of the experiment must be known. This is very difficult to measure and, though it can be readily calculated,[19] there is evidence that pulsed supersonic expansions do not necessarily conform to these expectations.[28] To eliminate this uncertainty, we report the state-to-state branching ratios, consistent with our previous work.[7,8,12,29,30]

3. Results

The low lying S_1 vibrations that are potential VET destination states from 6^1 are shown as an energy level diagram in Figure 1.[11,31] Up-pumping (endoergic transfer of energy to vibrational levels higher than 6^1) was not observed in our experiments. This confirms that the translational temperature is low in all cases, because endoergic transfer occurs only at higher temperature in the free jet.[32] The five destination levels that are lower in energy than 6^1 are 11^1, 16^2, 4^1, 16^1, and 0^0. The 11^1 and 16^1 levels give rise to bands that overlap in the dispersed fluorescence spectrum and they are treated as a combined relaxation channel in presenting the state-to-state branching ratios. Transfer of population to the other low lying vibrations can be distinguished unambiguously at the resolution used.

3.1. VET Spectra. Representative examples of time integrated dispersed fluorescence spectra are shown in Figure 2. From the spectra shown it can be seen that broad rotational contours are a feature of the VET growth bands, particularly 0^0, with these polyatomic collision partners. This was seen consistently with the polyatomic partners studied here. Broad contours were also observed in our previous study of polyatomic collision partners that could not participate in V → V transfer.[8]

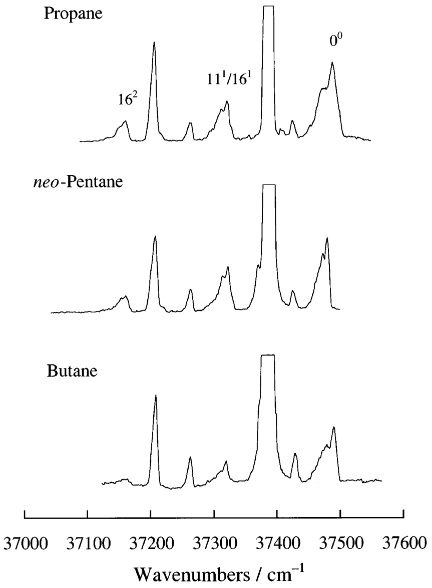

Figure 2. Time integrated dispersed fluorescence spectra of S_1 benzene (integrated between 0 and 400 ns after laser excitation of the 6^1 level) with the V → V collision partners propane (upper spectrum), neopentane (middle spectrum), and butane (lower spectrum). VET growth bands are identified by the emitting level in the upper spectrum.

TABLE 2: State-to-State Branching Ratios (%) for Transfer from 6^1 with Large Polyatomic Collision Partners[a]

	destination channel			
collision partner	4^1	16^2	$11^1/16^1$	0^0
CH_2Cl_2		11	40	49
C_2H_6		4	26	70
C_3H_8		12	25	63
n-C_4H_{10}		5	20	75
i-C_4H_{10}		4	36	60
c-C_5H_{10}		17	38	45
$(C_2H_5)_2O$		3	17	80
n-C_5H_{12}		4	17	79
i-C_5H_{12}		13	31	56
$C(CH_3)_4$		13	36	51
n-C_6H_{14}		12	13	75

[a] Branching ratio uncertainties are typically ±10%, measured as 2 standard deviations from the analysis of a minimum of three TRDF spectra.

A prominent 6^0_1 band is present in the VET spectra with all of the polyatomics studied here, indicating that transfer to 0^0 is an important relaxation pathway for these partners. In fact, it is the dominant relaxation pathway for the majority. Transfer to the unresolved $11^1/16^1$ channel is sometimes comparable to transfer to 0^0. The 16^2 channel plays a minor role.

3.2. State-to-State Branching Ratios. The relative rate coefficients for state-to-state transfer were obtained using the kinetic analysis described in ref 7. The relative rate coefficients for each channel, when normalized to their sum, give the relative efficiency of transfer to each of the different destination states, i.e., the state-to-state branching ratios. The state-to-state branching ratios for the different collision partners are presented in Table 2.

A key feature of the state-to-state branching ratios is the large fraction of transfer to 0^0 that occurs for all partners. For the majority of partners transfer to 0^0 is the dominant mechanism. This is unusual. For monatomic partners transfer to 0^0 is not observed whereas for diatomics and small polyatomics transfer to 0^0 is observed but, with the exception of H_2, is not the dominant channel.[7,8]

4. Discussion

4.1. Transfer to 0^0: Evidence for V → V Transfer. The first issue to be addressed is the mechanisms for vibrational relaxation that are operating. In particular, does the availability of vibrational levels below 522 cm^{-1} (the 6^1 vibrational energy) in the collision partner lead to V → V transfer occurring? The signature of V → V transfer in the data is an enhancement in the branching ratios for transfer to levels where V → V transfer is possible. There are a number of arguments that we believe point to V → V transfer being operative for the majority of the polyatomic partners studied here. We focus on transfer via the channel $6^1 \rightarrow 0^0$ because this is the dominant channel for most of these polyatomic partners (see Table 2).

First, we review what is known of vibrational relaxation for 6^1 benzene from previous work and use that to deduce the V → R,T transfer behavior expected for the present partners. The argument is that a significant shift from these predictions provides evidence for the need to invoke another transfer mechanism.

Experiments with the rare gas collision partners He, Ne, Ar, and Kr established that $6^1 \rightarrow 0^0$ transfer does not occur when V → T transfer is the only mechanism operating.[7] This appears to arise from angular momentum constraints.[8,33] The issue is that the probability of transferring 522 cm^{-1} of energy (the 6^1–0^0 energy gap) to translation is very low. This can be overcome by transferring energy to rotation, but for monatomic partners only benzene has internal rotation available. Conservation of angular momentum requires the benzene rotation to be balanced by orbital angular momentum and this constrains the extent of rotational excitation that can occur. The permitted rotational excitation is too low to significantly reduce the translational energy change and transfer to 0^0 is not competitive.

With diatomics and small polyatomics, transfer to 0^0 is observed because energy can be accommodated within rotations of both benzene and the collision partner (V → R transfer).[8] Generally it was found that the smaller the rotational constant of the collision partner, the smaller was the transfer to 0^0.[8] Transfer to 0^0 was largest for hydrogen because, having a rotational constant ~61 cm^{-1}, it can have large changes in rotational energy with minimal changes in angular momentum. Hydrogen is the only V → R partner studied for which the branching ratio for transfer to 0^0 is >45%. Indeed, if one ignores H_2 and D_2, which have particularly large rotational constants, the next largest branching ratio for transfer to 0^0 seen previously was 36% for methane, which for a polyatomic has a comparatively large rotational constant of ~5 cm^{-1}. Cyclopropane has a branching ratio to 0^0 of 25% whereas for acetylene the value is 12%.

Because the rotational constants of the polyatomic partners studied here are generally small, the transfer of large amounts of energy to rotation would require large changes in angular momentum. The evidence, both experimental and theoretical, is that this is unfavorable.[8,33] Consequently, it is expected that a V → R,T transfer mechanism will lead to 0^0 branching ratios less than those seen in our earlier study. A conservative estimate would be a value of 25% or less on the basis of the behavior of cyclopropane. Transfer to 0^0 in excess of this value would suggest that the additional mechanism of V → V transfer is operating. By allowing some of the energy to go into vibrational modes of the partner, V → V transfer provides another mechanism to reduce the translational energy gap.

Second, we consider the trends seen in the room temperature experiments on 6^1 benzene by Parmenter and Tang.[11] These experiments showed an enhancement in transfer to 0^0 by large polyatomic partners. This was interpreted as an indication of the involvement of V → V transfer for these partners. It follows that an enhancement in the $6^1 \rightarrow 0^0$ branching ratio in our experiments is consistent with the observations by Parmenter and Tang and, consequently, demonstrates that V → V transfer is operating at low temperature, as it was at room temperature.

These arguments lead to the conclusion that an enhancement in the $6^1 \rightarrow 0^0$ branching ratios for the present set of polyatomic partners would point to the involvement of a V → V mechanism. The state-to-state branching ratios for transfer to 0^0 seen here are significantly larger than those observed for the V → R,T polyatomics. The polyatomic V → R,T partners had 0^0 branching ratios less than 40% (methane 36%; cyclopropane 25%, acetylene 12%).[8] In contrast, *all* of the polyatomics studied here have branching ratios for transfer to 0^0 larger than this. Almost half (five of the 11 partners) have transfer to 0^0 >70%. Cyclopentane has the lowest transfer to 0^0, with a branching ratio of 45%. This behavior is in stark contrast to the case of *p*-DFB, where V → V,R,T polyatomics showed branching ratios similar to those for V → R,T polyatomics.[12] The most straightforward explanation for the large transfer to 0^0 is to ascribe it to V → V transfer. For those few partners where transfer to 0^0 is below 50%, it might be argued that a V → V mechanism need not be invoked; however, such an argument would need to account for why these partners do not fit the trends with the rotational constant seen previously. We propose that the significantly increased importance of 0^0 as a destination channel provides compelling evidence that V → V transfer is occurring for most, if not all, of the partners studied in this work.

It is particularly enlightening in this context to compare selected partner pairs for which large differences are not expected should V → V transfer be inoperative. Compare, for example, the partners propane ($M = 44$ amu) and ethane ($M = 30$ amu) with cyclopropane ($M = 42$ amu) and acetylene ($M = 26$ amu), respectively. All have quite small rotational constants compared with hydrogen, deuterium, and methane for which V → R transfer leads to significant population of 0^0 (in excess of 30%). For propane 65% of transfer occurs to 0^0 whereas for cyclopropane only 25% is via this channel. For the pair ethane/acetylene the difference is even more striking, with 70% transfer to 0^0 for ethane and only 12% for acetylene. These comparisons illustrate the significant increase in transfer to 0^0 that occur when V → V transfer is possible.

With such large differences between partners with similar mass it is interesting to note the collision partner dependence for energy transfer in glyoxal.[34] Here the vibrational and rotational transfer is sensitive primarily to the reduced mass of the collision and is the same for the collision pairs cyclohexane/krypton ($M = 84$ amu) and deuterium/helium ($M = 4$ amu). For the channels observed (loss and gain of ν_7), V → V transfer is highly unlikely because the lowest vibrational mode in cyclohexane is higher in energy than ν_7. This study was performed in a crossed molecular beam with collision energies of 700 and 2900 cm^{-1} (the former for He/D_2; the latter for Kr/cyclohexane), whereas our study involves collision energies typically less than 100 cm^{-1}.[7] Although it is not clear that the glyoxal trends extrapolate to our situation, these observations provide further evidence that the behavior of benzene with the polyatomic partners studied here is unusual in the context of V → R,T transfer.

Though the case for V → V transfer is circumstantial, there is sufficient evidence to make it compelling. Establishing V → V transfer directly requires experiments that monitor the growth in population of vibrational modes in the collision partner. Such experiments, which have been reported for small collision partners such as CO_2 in relaxation of highly excited polyatomics (see, for example, refs 35 and 36), provide the opportunity to gain insight into the transfer process through identifying the partner modes involved and are a potential future direction for this work.

4.2. Transfer to 16^2 and $11^1/16^1$. Besides 0^0, two other destination channels are observed, 16^2 and $11^1/16^1$. 16^2 is the least efficient of the observed vibrational relaxation channels, consistent with the required high vibrational quantum change, $|\Delta v|$, of 3. (The only other accessible level, 4^1, is not observed, as discussed in the following section.) The $11^1/16^1$ channel varies in its relative efficiency with the polyatomic colliders, largely according to the magnitude of transfer to 0^0: as the branching ratio for transfer to 0^0 decreases, the branching ratio for transfer to $11^1/16^1$ increases, and vice versa. The evidence from the rotational contours is that transfer to 16^1 dominates transfer to 11^1 (see section 4.5).

Our observation that $11^1/16^1$ remains much smaller than 0^0 is interesting in view of the possibility for near-resonant V → V transfer to 16^1 offered by some partners. Dichloromethane and cyclopentane each have a mode with frequency 283 cm^{-1}, very nearly resonant with the 6^1-16^1 energy gap of 285 cm^{-1}. The state-to-state branching ratios for $11^1/16^1$ are marginally the largest for these two partners, which have correspondingly lower 0^0 branching ratios. However, within experimental uncertainty neopentane and isobutane have the same branching ratio for transfer to $11^1/16^1$ as does cyclopentane, yet they do not have a vibrational mode isoenergetic with the 6^1-16^1 energy gap. This suggests that resonance is not a major factor. A similar conclusion was reached by Parmenter's group for resonant transfer involving $6^1 \rightarrow 0^0$.[11]

4.3. Absence of Transfer to 4^1. A feature common to the collision partner systems studied here and in our previous work is the absence of transfer to 4^1. We have now studied a range of collision partners, including monatomics,[7] diatomics and small polyatomics,[8] and now larger polyatomics. The only collision partner for which transfer to 4^1 was observed was H_2, and in that case the branching ratio was only 2%. Parmenter and Tang also noted an absence of transfer to 4^1 in their room temperature measurements.[11] They suggested that the apparent inefficiency of transfer to 4^1 may be due to a reduced fluorescence quantum yield from this state compared with the other destination levels. Later measurements of benzene fluorescence quantum yields by Stephenson and Rice[37] suggest that the fluorescence quantum yield for 4^1 is reduced compared to its neighbors but that the magnitude of the reduction is insufficient to explain the absence of observed transfer to 4^1. (The fluorescence quantum yield for 4^1 has not been measured, but the drop in quantum yield from 6^1 to 6^14^1 is ca. 30%.[37]) The prohibition on transfer to 4^1 cannot be energetic, because levels above and below 4^1 are populated. Similarly, the reason cannot be that the transfer involves $|\Delta v| = 2$, because other $|\Delta v| = 2$ transfer is observed (the $11^1/16^1$ channel).

There are no theoretical calculations for the particular case of VET in benzene to illuminate why 4^1 is not accessed. However, we note the close-coupled quantum-mechanical scattering calculations performed by Clary for the scattering of helium atoms from the 0_0 level of *p*-difluorobenzene.[38] These calculations examined geometrical characteristics of the transfer to the various accessible vibrational modes. When the vibrations were set to the same frequencies in the calculation, modes with atomic displacements out of the plane had larger vibrational excitation cross sections. In addition, the calculations found that the symmetry of each mode dictated the angle of approach for the most efficient vibrational excitation. These conclusions illustrate that geometric effects can be significant in collisions involving aromatic species.

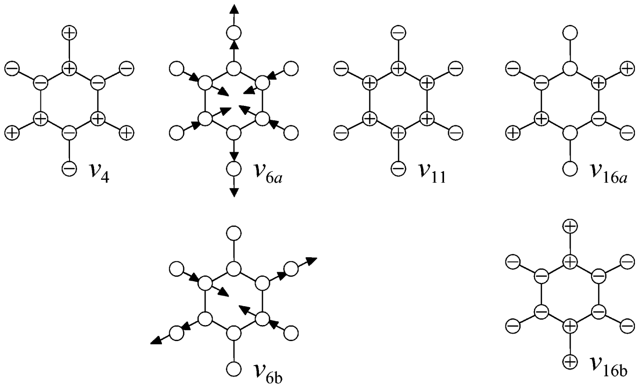

Figure 3. Schematic diagram of the atomic displacements for the normal mode vibrations of benzene for vibrational levels that may be involved in VET in the low temperature free jet expansion. ν_6 and ν_{16} are doubly degenerate.

The experimental evidence is that the atomic displacements involved in ν_4 are not easily excited in collisions that simultaneously de-excite ν_6. The vibrational motions of all the modes in benzene that are relevant to these studies are shown schematically in Figure 3.[39] The vibrational modes that may be excited during VET, ν_4, ν_{11}, and ν_{16}, are all out-of-plane vibrations whereas ν_6, the mode that must be de-excited, is in-plane. ν_4 is the only destination mode in which the carbon atoms situated on opposite sides of the benzene ring move in opposite directions. This differentiating feature of ν_4 is presumably what prevents its excitation. The changes in atomic motion that benzene molecules excited to ν_6 must undergo to de-excite and simultaneously initiate vibration in ν_4 must be prohibited for the majority of collision geometries.

4.4. Collision Partner Dependence of V → V Transfer. It is instructive to compare the extent of transfer to 0^0 by cyclopentane, dichloromethane, and ethane. These species have a single vibrational level capable of being involved in V → V transfer and the vibrational frequencies of these are very similar (283, 283, and 275 cm^{-1}, respectively). The branching ratios for transfer to 0^0 are 45%, 49%, and 70% for cyclopentane, dichloromethane, and ethane, respectively. Thus the partner's vibrational energy level structure appears to be irrelevant. Further evidence for this is that neopentane, with four vibrational modes below 6^1, shows a $6^1 \rightarrow 0^0$ branching ratio of 51%, comparable to cyclopentane and dichloromethane.

The experimental evidence shows that it is not essential for there to be a large number of accepting modes in the polyatomic collider for V → V transfer to play a role in the relaxation of 6^1 benzene, as witnessed by the behavior of ethane. Indeed, a large number of accessible vibrational modes does not guarantee significant V → V transfer, as seen by the behavior of branched and cyclic species in general, and neopentane in particular. The presence of a close resonance between a vibrational level in the collision partner and the 522 cm^{-1} 6^1-0^0 energy gap is likewise not essential. In fact, as we discuss in section 4.5, it is

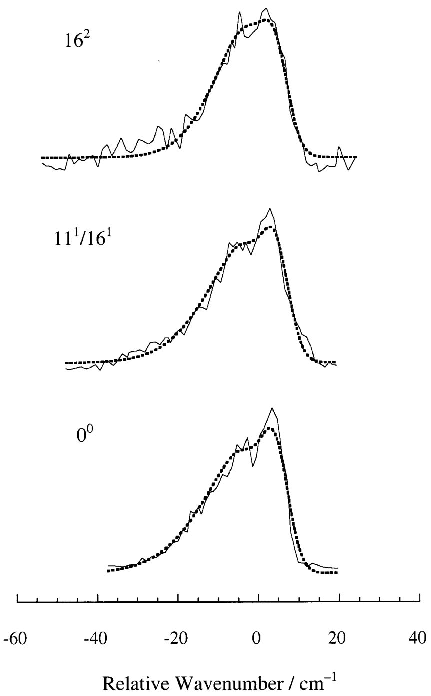

Figure 4. Fits to neopentane growth band rotational contours using thermal distributions for the rotational distributions in the destination vibrations: (a) the 6^0_1 band (b) the 6^0_1 $11^1_1/6^0_1$ 16^1_1 band and (c) the 6^0_1 16^2_2 band. The temperatures of best fit are 105, 95, and 70 K, respectively. The calculated spectra are dashed.

likely that low frequency acceptor modes are primarily involved, i.e., modes far from resonance.

Given the lack of correlation of V → V transfer with vibrational energy level structure, one of the interesting features of the data is that the straight chain species consistently show more transfer to 0^0 than branched species. The average branching ratio for transfer to 0^0 by the five straight chain alkanes is 72 ± 3% (the uncertainty given is the standard deviation). In comparison, the average for four branched and cyclic alkanes is 53 ± 3%. The "straight chain" species diethyl ether shows behavior analogous to straight chain alkanes: in fact, within experimental error, it exhibits branching ratios identical to those for the analogous straight chain alkane, *n*-pentane. In this context dichloromethane behaves as a branched alkane: within experimental error, its branching ratios are the same as the somewhat similarly shaped neopentane [$C(CH_3)_4$]. The data raise the interesting possibility that molecular shape plays a role in determining the extent of V → V transfer in this system. We speculate that it may be that collisions that excite torsional modes in the "straight chain" species are facile. Calculations are required to provide insight into the mechanism responsible.

4.5. Rotational Contours of VET Growth Bands. Following the same procedure adopted in our previous study of rotational effects in VET,[7,8] we have fitted rotational contours for a representative subset of collision partners by assuming a Boltzmann distribution of rotational population in the collisionally populated levels. The collision partners for which rotational contours were fitted were neopentane, propane, isobutane, and *n*-butane. We found previously when studying the diatomic and small polyatomic partners that thermal distributions generally gave an adequate fit of the 5 cm^{-1} resolution contours. The fits are indicative of the average *J*,*K* distribution in the destination level of benzene, and the use of a thermal fit does not imply that the distribution is necessarily Boltzmann. Examples of fits for neopentane are shown in Figure 4. The fits, through the temperature required to fit the contour, provide a means to quantify differences between the contours for various partners.

Rotational relaxation occurring within the initial and final vibrational levels is not likely to be a significant contributor to the observed contours. This can be discerned from the observation that the rotational contours of bands originating from the initially populated 6^1 level remain narrow. Because rotational relaxation within the original vibration does not spread the population to high *J*,*K* states, it is most unlikely to do so within the destination vibration. Thus rotational relaxation within the initial or final vibration is not responsible for the distribution of rotational levels that appear in VET growth bands following vibrational relaxation. The distributions are the result of the angular momentum changes that accompany the vibrational energy transfer.

As illustrated by the fits shown in Figure 4, the growth band shapes can be reasonably matched to a thermal distribution. There are some cases where such a distribution does not provide an adequate description of the population distribution of the emitting levels; however, the thermal distribution is adequate for the majority of cases.

For the diatomics and small polyatomics the temperature of growth bands arising from transfer to particular destination vibrations was found to increase with increasing ΔE from 6^1. For the larger polyatomics we find that the temperatures for the growth band contours uniformly decrease from 0^0 to $11^1/16^1$ to 16^2. This suggests that for the $11^1/16^1$ channel, transfer to 16^1 ($\Delta E = 285$ cm^{-1}) dominates transfer to 11^1 ($\Delta E = 7$ cm^{-1}).[8]

The $6^1 \rightarrow 0^0$ channel is the one most influenced by V → V transfer. The 0^0 rotational contours are fitted by temperatures in the range 100−200 K. These compare with 0^0 rotational temperatures for the non-V → V polyatomic partners methane, acetylene, and cyclopropane that were in the range 150−280 K. The V → V polyatomic partners have, on average, slightly lower 0^0 temperatures than the non-V → V polyatomics but still show significant rotational excitation of benzene. If V → V transfer resulted in significant vibrational excitation of the collision partner there would be little energy left for excitation of rotation. The observation of excitation in benzene rotation and, by conservation of angular momentum, also in the collision partner, suggests that the vibrations excited in the collision partner must be well below the 6^1 energy of 522 cm^{-1}.

4.6. Comparison with *p*-Difluorobenzene (*p*-DFB). Mudjijono and Lawrance have reported that there is no enhancement of VET in *p*-DFB by a V → V mechanism.[12] The two V → V polyatomic partners used in that study, ethane, and isobutane, have both been used here, and both exhibited the enhanced transfer to 0^0 characteristic of V → V transfer in benzene. Thus Mudjijono and Lawrance find a different situation for *p*-DFB to the one that we find for benzene. Our observations for benzene are consistent with those made at room temperature by Parmenter and Tang.[9−11] Interestingly, V → R transfer also appears to be inoperative in *p*-DFB[29] yet operates in relaxation of 6^1 benzene.[8]

Recent experiments on the dissociation of van der Waals molecules may shed light on this difference between *p*-DFB and benzene. van der Waals molecule dissociation has relevance to collision-induced energy transfer through the former being a "half-collision" process, albeit potentially involving a limited set of initial geometries. Our group has recently measured the translational energy release (TER) distributions for dissociation of *p*-DFB−Ar and benzene−Ar within their S_1 states.[40] The TER distributions are almost identical in the two systems. In the case of VET within *p*-DFB, the highest level studied was 6^1 and the 6^1-0^0 energy gap is 410 cm^{-1}. The 6^1-0^0 gap in benzene is 522 cm^{-1}. The TER distributions decrease by a factor of ~10 from 410 to 522 cm^{-1}. In the context of VET, if V → T transfer is enhanced by a similar factor for 6^1 *p*-DFB compared with 6^1 benzene, this would explain the differences in behavior for the two molecules. With the probability for V → T transfer reduced for the $6^1 \rightarrow 0^0$ channel in benzene because of the large energy gap, mechanisms such as V → R and V → V transfer that reduce the translational energy changes required come into play. The observation that for monatomic partners $6^1 \rightarrow 0^0$ transfer in benzene is absent[7] yet is the dominant channel in *p*-DFB[30] supports this interpretation.

5. Conclusions

We have measured the state-to-state VET branching ratios from 6^1 benzene with 11 complex polyatomic colliders (9 hydrocarbons, diethyl ether, and dichloromethane). The relative efficiency of transfer to the accessible levels is markedly different from the behavior observed earlier with monatomic, diatomic, and small polyatomic collision partners. This is most obviously displayed in significantly increased branching ratios for transfer to 0^0. This is taken to indicate that V → V transfer enhances the vibrational relaxation cross section for transfer to 0^0.

The branching ratios for transfer to 0^0 are found to be larger for straight chain species than for branched species. The rotational contours of collisionally populated levels reveal rotational excitation accompanying vibrational relaxation similar to, but on average somewhat less than, that observed previously for smaller, non-V → V transfer partners. The presence of significant rotational excitation in the destination level suggests that it is the low frequency modes of the collision partner that are being vibrationally excited in the V → V transfer. We have noted the presence of V → R and V → V transfer for 6^1 benzene where they are absent for *p*-DFB. On the basis of the translational energy release distributions for van der Waals molecule dissociation, we suggest that this may be a consequence of the reduced probability of V → T transfer associated with the higher 6^1 energy in benzene. A reduction in the probability of V → T transfer leads to V → R and V → V transfer becoming competitive with V → T transfer.

Acknowledgment. This work was undertaken with the financial support of the Australian Research Council and Flinders University. We are grateful for the technical support provided by the staff of the School of Chemistry, Physics and Earth Sciences Engineering and Electronic Workshops. E.R.W. thanks Flinders University for the award of a Research Scholarship.

References and Notes

(1) Parmenter, C. S. *J. Phys. Chem.* **1982**, *86*, 1735.
(2) Krajnovich, D. J.; Parmenter, C. S.; Catlett, D. L., Jr. *Chem. Rev.* **1987**, *87*, 237.
(3) Rice, S. A. *J. Phys. Chem.* **1986**, *90*, 3063.
(4) Flynn, G. W.; Parmenter, C. S.; Wodtke, A. M. *J. Phys. Chem.* **1996**, *100*, 12817.
(5) Catlett, D. L., Jr.; Parmenter, C. S.; Pursell, C. J. *J. Phys. Chem.* **1994**, *98*, 3263.
(6) Catlett, Jr.; D. L.; Parmenter, C. S.; Pursell, C. J. *J. Phys. Chem.* **1995**, *99*, 7371.
(7) Waclawik, E. R.; Lawrance, W. D. *J. Chem. Phys.* **1995**, *102*, 2780.
(8) Waclawik, E. R.; Lawrance, W. D. *J. Chem. Phys.* **1998**, *109*, 5921.
(9) Atkinson, G. H.; Parmenter, C. S.; Tang, K. Y. *J. Chem. Phys.* **1979**, *71*, 68.
(10) Tang, K. Y.; Parmenter, C. S. *J. Chem. Phys.* **1983**, *78*, 3922.
(11) Parmenter, C. S.; Tang, K. Y. *Chem. Phys.* **1978**, *27*, 127.
(12) Mudjijono; Lawrance, W. D. *J. Chem. Phys.* **1996**, *105*, 9874.
(13) Herzberg, G. *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1945.
(14) Snyder, R. G. *J. Chem. Phys.* **1967**, *47*, 1316.
(15) Derreumaux, P.; Daechez, M.; Vergoten, G. *J. Mol. Struct.* **1993**, *295*, 203.
(16) Lifson, S.; Warshel, A. *J. Chem. Phys.* **1968**, *49*, 5116.
(17) Snyder, R. G. *Spectrochim. Acta* **1967**, *23A*, 391.
(18) Mirkin, N. G.; Krimm, S. *J. Phys. Chem.* **1993**, *97*, 13887.
(19) Miller, D. R. In *Atomic and molecular beam methods*; Scoles, G., Ed.; Oxford University Press: Oxford, U.K., 1988; Vol. 1.
(20) Jouvet, C.; Sulkes, M.; Rice, S. A. *Chem. Phys. Lett.* **1981**, *84*, 241.
(21) Yoder, L. M.; Barker, J. R. *Phys. Chem. Chem. Phys.* **2000**, *2*, 813.
(22) Gotch, A. J.; Zwier, T. S. *J. Chem. Phys.* **1992**, *96*, 3388.
(23) Shelley, M. Y.; Dai, H.-L.; Troxler, T. *J. Chem. Phys.* **1999**, *110*, 9081.
(24) Carrasquillo, E.; Zwier, T. S.; Levy, D. H. *J. Chem. Phys.* **1985**, *83*, 4990.
(25) Hopkins, J. B.; Powers, D. E.; Smalley, R. E. *J. Phys. Chem.* **1981**, *85*, 3739.
(26) Law, K. S.; Shauer, M.; Bernstein, E. R. *J. Chem. Phys.* **1984**, *81*, 4871.
(27) Sampson, R.; Lawrance, W. D. Unpublished results.
(28) Zou, B. S.; Dudukovic, M. P.; Mills, P. L. *Rev. Sci. Instrum.* **1993**, *64*, 3492.
(29) Mudjijono; Lawrance, W. D. *J. Chem. Phys.* **1996**, *105*, 3019.
(30) Mudjijono; Lawrance, W. D. *J. Chem. Phys.* **1996**, *104*, 7444.
(31) Swiderek, P.; Holneicher, G.; Maluendes, S. A.; Dupuis, M. *J. Chem. Phys.* **1993**, *98*, 974.
(32) Moss, D. B.; Kable, S. H.; Knight, A. E. W. *J. Chem. Phys.* **1983**, *79*, 2869.
(33) McCaffery, A. J.; Marsh, R. J. *Phys. Chem. Commun.* **2001**, *24*, 1.
(34) Gilbert, B. D.; Parmenter, C. S.; Krajnovich, D. J. *J. Chem. Phys.* **1994**, *101*, 7440.
(35) Mullin, A. S.; Michaels, C. A.; Flynn, G. W. *J. Chem. Phys.* **1995**, *102*, 6032.
(36) Park, J.; Shum, L.; Lernoff, A. S.; Werner, K.; Mullin, A. S. *J. Chem. Phys.* **2002**, *117*, 5221.
(37) Stephenson, T. A.; Rice, S. A. *J. Chem. Phys.* **1984**, *81*, 1073.
(38) Clary, D. C. *J. Chem. Phys.* **1987**, *86*, 813.
(39) Stephenson, T. A.; Radloff, P. L.; Rice, S. A. *J. Chem. Phys.* **1984**, *81*, 1060.
(40) Bellm, S. M. Ph.D. Thesis, Flinders University, Adelaide, South Australia, 2001.