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Gateway Modes in the Collisional Energy Transfer from Highly Vibrationally Excited CS_2

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The role of different vibrational modes in the energy transfer from highly vibrationally excited CS_2 is investigated in model classical trajectory calculations. The primary tool for this work involves determining the dependence of the average energy transfer on the vibrational frequency of each mode. These calculations show that the energy transfer is highly sensitive to the frequency of the bend and the symmetric stretch mode. By increasing or decreasing the bend frequency the efficiency of the energy transfer decreases or increases, respectively. Variation of the symmetric stretch frequency causes a comparable effect. Variation of the asymmetric stretch mode frequency can lead to activation of energy transfer only if the frequency of the other two modes is made so high that the energy transfer through those modes becomes negligible. If the vibrational frequencies of highly excited CS_2 are set to their “natural” values, the bending mode is the conduit through which the energy “leaks out” of the molecule, similarly to the slightly excited molecule. Bending is the gateway mode not only because it is the lowest frequency mode but also because of the shape of the molecule: a sideways attack, which is much more probable than an axial attack, always interacts with the bend mode but only to a small extent with the asymmetric stretch mode, independently of the actual frequencies. The activity of a mode in energy transfer is determined mostly by its frequency, but the nature of the motion of the atoms involved in the mode also play a role.

I. Introduction

Collisional energy transfer from highly vibrationally excited polyatomic molecules received considerable attention in the last couple of years[1−10] since this is the way how energy flows between molecules in the gas phase before and after reactions or external excitation. In the earlier experiments the rate of energy transfer was studied using, as a reference, some unimolecular chemical reactions competing with energy transfer.[10−15] The evaluation of these experiments was done via model calculations: the master equation describing the process was solved and the parameters characterizing the energy transfer were varied until agreement with the experiment was found. The resolution of these experiments, even with the introduction of the more refined chemical activation studies, is limited as the results showed limited sensitivity to the details of the energy transfer rate coefficients. The development of spectroscopic techniques opened a way to follow the population of energy levels of either the highly excited molecules or the collision partner in real time.[1−4,16−22]

Although a large amount of experimental data was collected during the past few years, the general rules governing the energy transfer remained unclear. Theoretical calculations supporting the experiments are also needed. Because of the large number of internal modes and/or open channels in the collisional energy transfer involving a polyatomic molecule, quantum scattering calculations have a limited range of applicability[23−26] in this field. One may expect, however, that at the high densities of states characterizing the large, highly vibrationally excited polyatomic molecules, classical trajectory methods may help to understand the mechanistic details of energy transfer. The technology needed for such calculations involves the machinery of Monte Carlo classical trajectory methods developed and applied earlier for reactive and nonreactive collisions of small molecules[27,28] with some modifications specific to inelastic collisions involving polyatomic molecules.[29−32] These methods are widely used[33−46] for the modeling of collisional energy transfer. Tests of classical trajectories against accurate quantum scattering calculations showed good agreement of the average quantities,[31,42,43] and the average energy transfers were found to be in reasonable agreement with the experiment.[31,39,44] The classical mechanical methods can help us to understand details of the energy transfer like the energy and temperature dependence of the energy transfer probabilities[38,45] or the average duration of the collision,[34,40,41] effects of the intermolecular force field,[44,46,47] and other details.

An interesting question that has remained open is what are the properties of the excited molecule that determine the efficiency of energy transfer. In this paper we present results obtained from classical trajectory calculations devoted to answer the question: how important are the properties of each mode in determining the efficiency of energy transfer from a highly vibrationally excited molecule? The generally accepted picture is that energy is transferred through some gateway modes to and from the excited molecules, namely, through low-frequency modes[48−50] (which are, in actual molecules, usually bending modes). The basis of this statement is the large body of experimental data on energy transfer from large molecules having low enough vibrational energy to allow state-to-state experiments. The experiments show that the probability of losing a quantum from a low-frequency bend mode is larger than that from stiff modes. In more recent theoretical work, Koifman et al.[51] proposed that in SO_2 rare gas collisions at low excitation the energy is transferred from SO_2 through the “active” rotational mode corresponding to the projection of the total angular momentum of the molecule on the principal axis corresponding to the smallest moment of inertia. Dashevskaya et al.[52,53] developed a model based on the assumption that atom−atom encounters during collisions are adiabatic. If the conditions for adiabaticity are satisfied, the largest transition probability is expected if the frequency of a relaxing mode is low.[51,53]

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In their analysis of the mechanism of supercollisions[54-56] in toluene, Clary et al.[57] found that multiquantum transitions occur with relatively large cross section if out-of-plane bending modes are excited. From inspection of the trajectories corresponding to some individual supercollisions, they concluded that in supercollisions energy leaves the molecule through an out-of-plane bending mode. Reduced dimensionality quantum scattering calculations showed that the probability of multiquantum transitions is generally larger for a lower frequency mode.[25,26,42,43] In our preliminary work on the energy transfer from CS_2 we found that the average energy transferred per collision is very sensitive to the frequency of the bending mode.[58] It is not clear, however, whether only the frequency of the possible gateway modes controls the efficiency of the energy transfer or the nature of the motion involved in the vibration in question also influences it. In other words, are the low-frequency bending vibrations the gateway modes because they have low frequencies, or does the bending nature of the motion also help?

In this paper we report trajectory calculations on the energy transfer from the model molecule CS_2, a system we have extensively studied before.[30,31,38,47,55,59] In principle, the precise method for assigning which modes are active in the energy transfer would be that one calculates the analogues of the quantum state-to-state transition probabilities. These can in principle be calculated by extending the methods used in quasiclassical trajectory calculations involving diatomic molecules. In a polyatomic molecule, the amplitudes of the various modes can, in principle, be analyzed and the good action variables that correspond to vibrational quantum numbers[60-62] can be determined. An investigation of the temporal evolution of normal and local mode coordinates of our model, highly excited CS_2, however, showed that high excitation of these coordinates does not produce quasiperiodic oscillations, so action variables cannot easily be assigned to them. The oscillations we observed at high excitation very often carry the signs of chaotic intramolecular motion. As a result, even though the good action calculations can be useful at low excitation, they cannot help to clarify the mechanism of energy transfer from highly excited molecules. We have therefore chosen another way to identify the active modes in the energy transfer: we systematically modify the frequencies of the normal modes of CS_2 and observe the consequences by monitoring the change in the average energy transfer, $\langle \Delta E \rangle_{\text{vib}}$. We consider $\langle \Delta E \rangle_{\text{vib}}$ as a measure of the efficiency of the energy transfer process. We also study the energy transfer probability distributions. Section II briefly reviews the methods and the details of the control of frequencies. In section III we present the results and in section IV how we interpret them.

TABLE 1: Parameters of the Force Field and the Corresponding Normal Mode Frequencies[a]

f_{bend} mdyn Å rad^{-1}	$\beta_{\text{C-S}}$/Å^{-1}	$\beta_{\text{S-S}}$/Å^{-1}	ν_{bend}/cm^{-1}	ν_{ss}/cm^{-1}	ν_{as}/cm^{-1}
0.577 22	2.3875	1.1238	400.8	674	1532
0.144 305	2.3875	1.1238	200.4	674	1532
9.235 52	2.3875	1.1238	1603.2	674	1532
0.577 22	1.1937	5.1004	400.8	1348	766
0.577 22	1.1937	2.3371	400.8	674	766
0.577 22	1.1937	0.5625	400.8	337	766
0.577 22	0.5969	2.5522	400.8	674	383
0.577 22	0.2984	2.6030	400.8	674	191.5
0.144 305	1.1937	2.3371	200.4	674	766
2.308 8	1.1937	2.3371	200.4	674	766
0.577 22	2.3875	4.6717	400.8	1348	1532
0.577 22	4.775	4.6717	400.8	1348	3064
9.235 52	2.3875	4.6717	1603.2	1348	1532
9.235 52	2.3875	2.3371	1603.2	1348	766
9.235 52	0.5969	5.2040	1603.2	1348	383
8.435 52	0.6246	2.5455	1532	674	400.8
8.435 52	1.0503	1.1594	1532	400.8	674
0.577 22	1.0503	5.8622	400.8	1532	674

[a] The other Morse oscillator parameters are $r_{\text{e,C-S}} = 1.553$ Å, $D_{\text{e,C-S}} = 88.319$ kcal mol^{-1}; $r_{\text{e,S-S}} = 3.106$ Å, $D_{\text{e,S-S}} = 45.0$ kcal mol^{-1}.

II. Methods

We use the machinery developed earlier for the calculation of quantities characterizing energy transfer. The average vibrational, rotational and translational energy transferred per collision as well as the energy transfer probability distribution are determined by the single energy collision method.[29-31] Briefly, the classical equations of motion are calculated for a large number of collisions. The initial vibrational and rotational energy are set to the same predetermined value at the beginning of each collision. The phase space of the excited molecule is sampled microcanonically. The initial relative coordinates and momenta for the collision partners are selected using Monte Carlo methods from a thermal ensemble. The parameters of the collision partner, CO, are sampled using the classical description of a rotating-vibrating Morse oscillator.[28] The total energy of CS_2 was separated into vibrational and rotational parts using the procedure developed by Bruehl and Schatz.[29] In this method the rotational energy is obtained from the angular momentum component perpendicular to the instantaneous plane of the molecule, and the vibrational energy is calculated by subtracting E_{rot} from the total energy of the molecule. This way the contribution from the l quantum number ("the nonadiabatic part of the rotation energy" in the terminology of Koifman et al.[51]) is counted as vibrational energy.

The model molecule from which energy is transferred, CS_2, is a linear molecule with experimental vibrational frequencies 401 cm^{-1} (doubly degenerate bend), 658 cm^{-1} (symmetric stretch), and 1535 cm^{-1} (asymmetric stretch).[63] We represent the force field of the molecule by three Morse oscillators for the two C−S and the S−S interactions and a harmonic bend potential for the S−C−S bend mode (see ref 29). The parameters of these functions taken from earlier modeling are listed in the first line of Table 1, and yield frequencies of 401, 674, and 1532 cm^{-1} for the bend, symmetric stretch and asymmetric stretch modes, respectively. This force field is easily modified so that new vibrational frequencies are obtained while the dissociation energies remain unchanged. By changing the bend force constant by a factor of α, the bending frequency can be varied by a factor of $\alpha^{1/2}$, independently of the stretch modes. This way CS_2 with bending frequencies of 100, 200, 283, 401, 603, 1134, and 1604 cm^{-1} was created. Table 1 shows the modified parameters and the resulting frequencies. Independently of the bending mode, the frequencies for the asymmetric stretch mode were also modified to one-half, 766 cm^{-1}, and twice the original value, 3064 cm^{-1}. The present force field does not allow independent variation of the symmetric stretch frequency. The symmetric stretch frequency can be reduced below 401 cm^{-1} (the frequency of the bend mode in "regular" CS_2) only if the asymmetric stretch frequency is also reduced. To compare the effect of the reduction of the symmetric stretch frequency with that of the bending mode, we performed a series of calculations in which the asymmetric stretch frequency is 766 cm^{-1}, and the symmetric stretch and/or bend frequencies are halved or doubled as compared to the realistic model of CS_2. Note that the frequencies reported are harmonic normal-mode frequencies. At high excitation the normal mode description is far from the real motion of atoms in the molecule. In addition, it is clear that the phase space of the molecule may be quite different (like the onset of chaos,

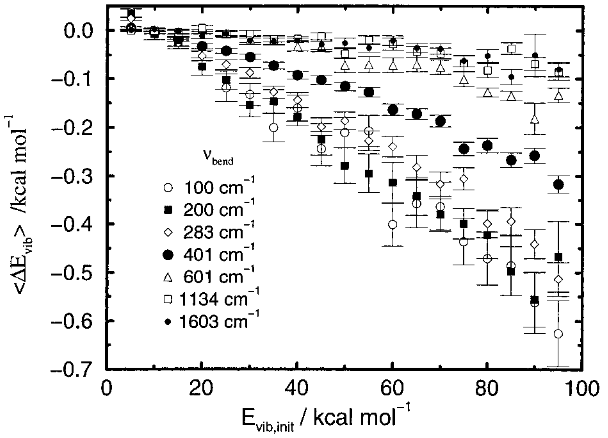

Figure 1. Average vibrational energy transferred from hot CS_2 molecules to a heat bath of CO molecules at 1000 K as a function of the initial vibrational energy in CS_2 at various bending frequencies of CS_2. The frequencies of the stretch modes are $\nu_{ss} = 674$ cm^{-1} and $\nu_{as} = 1532$ cm^{-1}.

location and extent of quasiperiodic orbits etc.) if the force field is modified. Despite their lack of complete accuracy, the harmonic frequencies seem to be a reasonable way to characterize the various force fields.

In the calculations of collisional energy transfer we used CO as a collision partner: it is not as simple as a rare gas atom, and an extensive set of data has been collected on CS_2 + CO before.[47,59] The temperature of the internal energy of the collision partner and the translational bath was taken to be 1000 K. The initial rotational energy of the hot CS_2 molecules was set equal to the thermal average value at 1000 K. The Monte Carlo trajectory calculations provide average energy transfers with nonnegligible error. Instead of calculating the characteristics of the energy transfer at a single energy, we found that it is safer to calculate them at several energies so that the tendencies become more visible. Accordingly, 2000 collisions were run at each of 19 initial energies at each set of vibrational frequencies. Energy transfer probability distributions are also derived in a few cases. For that purpose a larger number of collisions (10 000) were run at the same initial energy.

III. Results

The average vibrational energy transferred per collision from the hot CS_2 molecules calculated at seven different bending frequencies as a function of the initial vibrational energy in CS_2 is given in Figure 1. The stretch mode frequencies are kept fixed at 674 and 1532 cm^{-1}. The average energy loss from CS_2 increases faster than, but close to linear with the increase of the initial excitation energy, if the normal-mode frequencies are set to the experimental values (filled circles). As one makes the bending mode looser by decreasing its frequency, an increase of the absolute value of the average energy transferred from the hot CS_2 can be observed. The largest increase is observed when ν_{bend} is decreased by a factor of $2^{1/2}$: then $|\langle \Delta E\rangle_{vib}|$ increases by about a factor of 2 at high excitation. Further decrease of the frequency by factors of 2 and 4 also leads to more and more efficient energy transfer but the rate of change becomes slower. In complete agreement with these observations, if the bending mode is made stiff, the average energy loss from CS_2 decreases. If ν_{bend} is increased by a factor of 1.5, the average vibrational energy loss from the hot molecules decreases by about a factor of 2 (at or above $E_{init} \approx 40$ kcal mol^{-1}. Making the bend mode even stiffer seems to decrease the efficiency of energy transfer further but the absolute value of $\langle \Delta E\rangle$ is so small that, because of the statistical error, the rate of change is hard to evaluate.

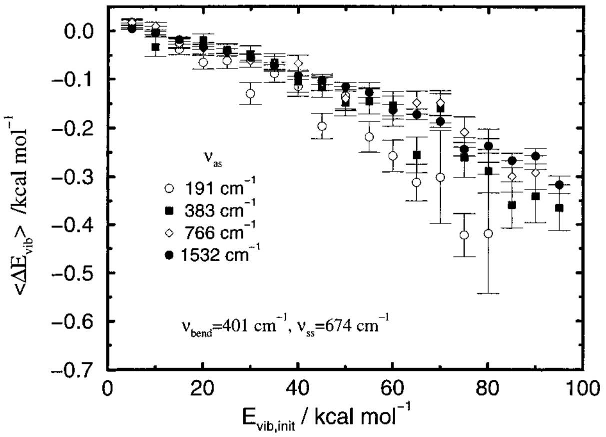

Figure 2. Average vibrational energy transferred from hot CS_2 molecules to a heat bath of CO molecules at 1000 K as a function of the initial vibrational energy in CS_2 at various frequencies of the asymmetric stretch mode. The frequencies of the other modes are $\nu_{bend} = 401$ cm^{-1} and $\nu_{ss} = 674$ cm^{-1}.

The calculations show that if the molecule has a low-frequency vibrational mode, the energy transfer becomes more efficient. To see whether the mode must be a bending mode or other types of motion can also facilitate the energy transfer, we varied the frequency of the other modes keeping the bend frequency fixed.

The asymmetric stretch frequency of 1532 cm^{-1} can be varied with our model potential independently of the bending mode but the range is limited as the symmetric stretch also varies if one changes the Morse exponential parameter β for the C−S mode. Figure 2. shows the effect of the variation of ν_{as} on the efficiency of the energy transfer. If one halves the asymmetric stretch frequency, the average energy transferred per collision hardly changes indicating that this mode is not active in the energy transfer. Decreasing ν_{as} further to 383 cm^{-1} (which is lower than that of the bend mode) still does not cause any significant change in the pattern of the $\langle \Delta E_{vib}\rangle$ vs E dependence. An enormous decrease by a factor of 8 to 191.5 cm^{-1} is needed to cause an observable increase of the efficiency of the energy transfer. At this value the frequency of the asymmetric stretch mode is way below that of the next lowest frequency mode, the bend mode. Larger effects can be observed, if the asymmetric stretch frequency is varied when the energy transfer through the other two modes is frozen by increasing the frequencies of both the bending and symmetric stretching modes to a high value. Figure 3 shows the changes of $\langle \Delta E_{vib}\rangle$ when $\nu_{bend} = 1603$ cm^{-1} and $\nu_{ss} = 1348$ cm^{-1}. In this case the average energy transfer is very small if the asymmetric stretch frequency is as high as in “natural” CS_2. This is in agreement with the observation made in conjunction with Figure 1, namely, that a large increase of the bending frequency will lead to a deactivation of the energy transfer. In contrast to Figure 2, however, in Figure 3 we can see that a decrease of ν_{as} by a factor of 2 does lead to an observable increase of the efficiency of energy transfer.

The symmetric stretch frequency cannot be selected completely freely when one applies our model potential. We studied its effect in a model molecule in which the asymmetric stretch frequency is one-half (766 cm^{-1}) of the “natural” value and the bending frequency is kept at the “natural” value (401 cm^{-1}). We have seen in Figure 2 that if the asymmetric stretch frequency is one-half of that in “regular” CS_2, the efficiency of energy transfer is essentially the same as in the “regular”

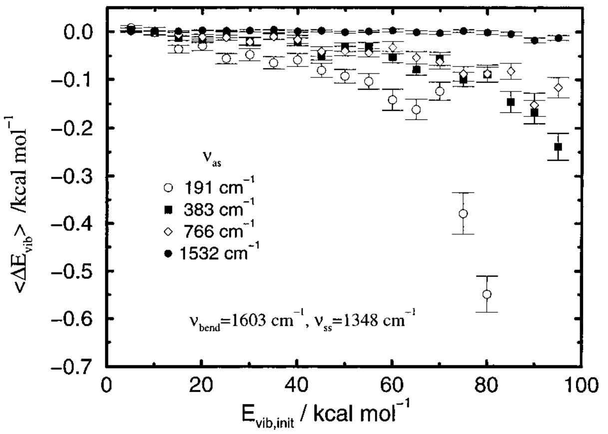

Figure 3. Average vibrational energy transferred from hot CS_2 molecules to a heat bath of CO molecules at 1000 K as a function of the initial vibrational energy in CS_2 at various frequencies of the asymmetric stretch mode. The frequencies of the other modes are ν_{bend} = 1603 cm^{-1} and ν_{ss} = 1348 cm^{-1}.

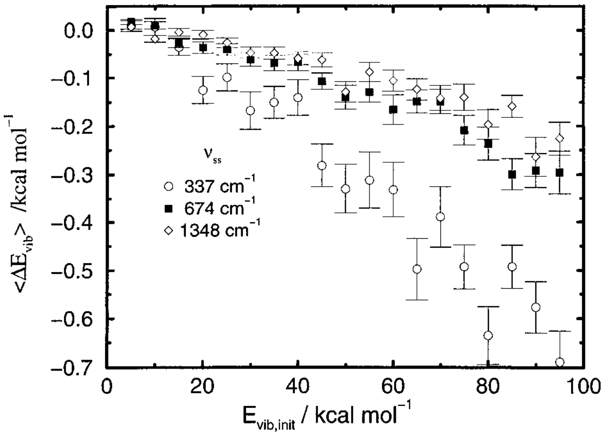

Figure 4. Average vibrational energy transferred from hot CS_2 molecules to a heat bath of CO molecules at 1000 K as a function of the initial vibrational energy in CS_2 at various frequencies of the asymmetric stretch mode. The frequencies of the other modes are ν_{bend} = 401 cm^{-1} and ν_{as} = 766 cm^{-1}.

molecule. Because of this we may assume that the changes that can be observed when varying the symmetric stretch frequency at this value of ν_{as} will also be valid for the "natural" molecule. The average energy transfers obtained when ν_{ss} is varied are plotted in Figure 4. The variation of the symmetric stretch frequency influences the energy transfer in the same way as that of the bending frequency does. When ν_{ss} is doubled, making the frequency of the symmetric stretch mode the highest in the molecule (1348 cm^{-1}), the average energy transfers drop by about 20%. If, on the other hand, ν_{ss} is decreased by a factor of 2, the average energy transfer becomes approximately 2.5 times larger.

The results show that the lowering of not only the bending frequency but also of the other modes will facilitate the energy transfer. The next question is whether the reduction of the frequencies of various modes promotes the energy transfer equally well or there are some preferred modes.

Figure 5 shows what happens if the same frequencies are redistributed among the modes. The most efficient vibrational energy transfer occurs when the bend, symmetric stretch, asymmetric stretch frequencies are set to 1532, 401, and 674 cm^{-1}, respectively, i.e., when the symmetric stretch is the lowest frequency mode. (The other permutation of the frequencies among modes with ν_{ss} = 401 cm^{-1} cannot be set with the model potential we used). The least efficient is the energy transfer if the lowest frequency is assigned to the asymmetric stretch mode. This is in agreement with the observation we made with respect to Figures 2 and 3. Taking into account all the available information, the asymmetric stretch mode seems to be much less efficient in the energy transfer than the other two modes.

The relative efficiency of the bending and symmetric stretch modes of CS_2 in activating the energy transfer was studied by comparing the relative effect of increasing or decreasing the frequency of one or the other mode. Figure 6 shows how the efficiency of the energy transfer changes when the frequencies of the modes, one by one, are reduced by a factor of 2. The reference case is ν_{bend} = 401 cm^{-1}, ν_{ss} = 674 cm^{-1}, and ν_{as} = 766 cm^{-1}. If the bending frequency is halved, the magnitude of the vibrational energy transfer increases by about a factor of 2. If, instead, the symmetric stretch frequency is decreased to 337 cm^{-1} (in this case this is the lowest frequency mode in the molecule), the average energy loss increases by about a similar factor, at some initial energies about 10% larger than that. The decrease of the asymmetric stretch frequency to 383 cm^{-1} causes a hardly visible increase of the efficiency of the energy transfer even though in this case this mode has the lowest frequency of the molecule. On the other hand, if the frequency of the modes

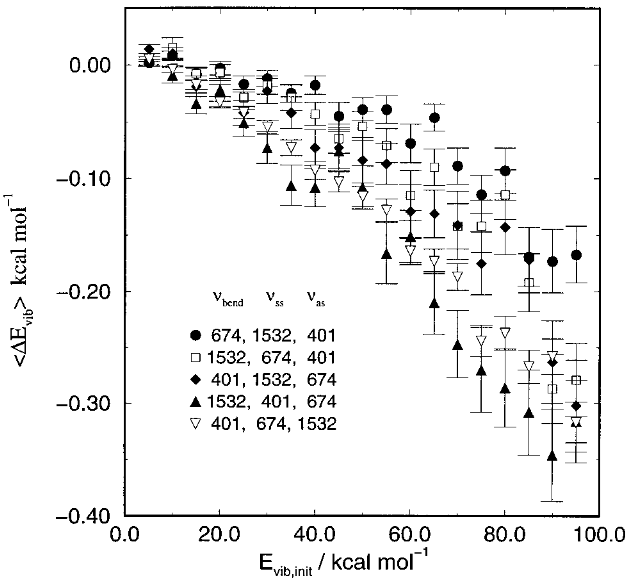

Figure 5. Effect of interchanging the mode frequencies of hot CS_2 molecules on the average vibrational energy transferred to a heat bath of CO molecules at 1000 K as a function of the initial vibrational energy in CS_2.

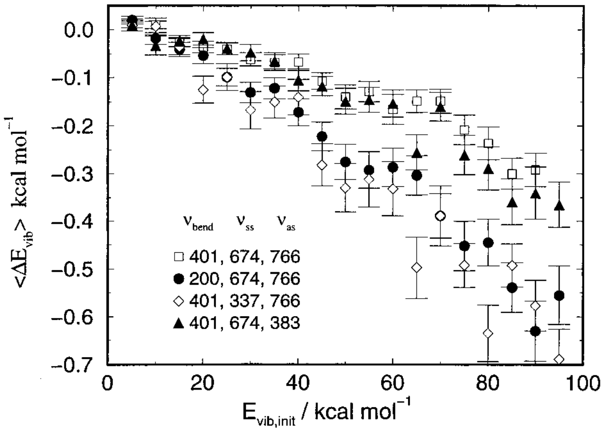

Figure 6. Effect of the reduction of the mode frequencies of hot CS_2 molecules on the average vibrational energy transferred to a heat bath of CO molecules at 1000 K as a function of the initial vibrational energy in CS_2.

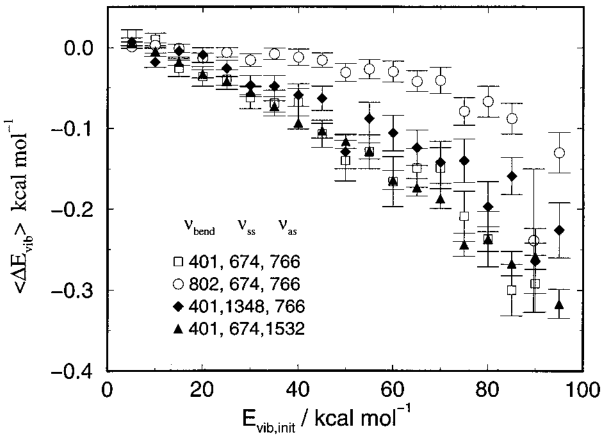

Figure 7. Effect of the increase of the mode frequencies of hot CS_2 molecules on the average vibrational energy transferred to a heat bath of CO molecules at 1000 K as a function of the initial vibrational energy in CS_2.

is doubled, the energy transfer is suppressed if the bend mode is made stiffer, while the effect of the stretch modes is smaller (Figure 7). If the bend frequency is increased from 401 to 802 cm^{-1}, the magnitude of the average energy transfer decreases by a factor of 3 or more. The increase of ν_{ss} causes about 20% decrease of $\langle \Delta E \rangle_{vib}$, while when the asymmetric stretch frequency is doubled, the efficiency of the energy transfer essentially does not change (note that in the latter two cases the bend mode frequency is lower than that of either of the stretch modes). At other combinations of ν_{bend} and ν_{ss} higher sensitivity to the bend mode frequency is observed if that was and remains the lowest frequency mode. Similarly, the average vibrational energy transfer is more sensitive to changes of the symmetric stretch mode frequency if that is the lowest frequency mode both before and after the modification.

The nature of the collision partner, in principle, can also influence the "mode specificity" of the energy transfer. The collision partner applied in the calculations reported above is CO, a diatomic molecule. In order to eliminate the possible effects of the internal degrees of freedom of CO, we performed calculations with an artificial collision partner that behaves like the "unified atom" model of CO: it has a mass of CO, and the atom−atom interaction potentials are the same as between O and S as well as O and C (which is in our model is identical to the C−S and C−C interaction: for both pairs we use the parameters of the Ne−Ar and Ne−Ne Lennard-Jones potential). The results of these calculations show that the qualitative observations, and in all cases the actual numbers (taking into account the statistical error of the calculations) are very similar to the results obtained with the diatomic CO.

IV. Discussion

A general conclusion from the trajectory data is that the efficiency of the energy transfer increases if the frequency of a mode is decreased. This is very clearly seen in the case of the bending mode of CS_2: increase of its frequency will deactivate the energy transfer of the molecule and vice versa. The reason why this is so clearly manifested is that this mode has the lowest frequency in this molecule. Activation of the energy transfer by a decrease of the asymmetric stretch frequency can hardly be seen, if the bend and symmetric stretch frequencies are low (Figure 2). The activation becomes more visible when ν_{as} is varied by setting high frequencies for the two other modes (Figure 3). The physical reason for this is that the other two modes become deactivated, so that the only way the energy transfer can take place is through the mode that has the lowest frequency even though that was the least efficient mode in "natural" CS_2. The activating effect of the decreased symmetric stretch frequency can be observed even if the bending frequency is low.

The observation that a mode with a smaller frequency is more active in the energy transfer is in very good accord with the results of the quantum scattering calculations. Reduced dimensionality studies of energy transfer from CS_2 were performed in two model systems: in collinear collisions of CS_2 with He, when the two stretch modes of CS_2 are considered,[25,42] and collisions in a T-shaped arrangement when the bend and symmetric stretch mode was coupled.[43] We found in both cases that the state-to-state inelastic scattering probabilities are larger for that mode which has the smaller frequency (symmetric stretch in the former and bend in the latter case).

The information concerning the effect of the change of the efficiency of the energy transfer caused by the variation of the frequencies of various modes helps us to identify the modes through which the energy transfer from CS_2 takes place. The most active mode in "natural" CS_2 is the lowest frequency mode, the bending vibration. The efficiency of the energy transfer is most sensitive to the changes of the frequency of this mode. If the frequency of this mode is made high, the average energy transfer decreases significantly indicating that the energy transfer becomes much less efficient while a decrease of this frequency activates the energy transfer. A more precise measure of the efficiency of the energy transfer is the magnitude of the probability of transferring energy from level E to level E', $P(E',E)$, or in a more global context, the width of the entire probability distribution at a fixed initial energy E'. The larger are the individual probabilities at nonzero energy transfer $E' - E$, the more efficient is the collisional energy transfer. At the same time, the larger are these probabilities, the wider is the distribution $P(E',E)$. (A small value of the average energy transfer could occur when the two wings of the distribution balance each other, even if both are wide, i.e., energy transfer is very efficient.) To test whether the average energy transfer adequately represent the efficiency of the energy transfer, we calculated $P(E',E)$ at various bending frequencies. 10,000 trajectories were run at initial energy $E = 95$ kcal mol^{-1} in CS_2 at each of $\nu_{bend} = 100$, 200, 401, 802, and 1603 cm^{-1}. Figure 8 shows the energy transfer probabilities P(E′,E) as a function of the energy gap, $E' - E$. The looser the bend mode, the wider are the distributions. Considering a given final energy, E′, one can see that the probability of getting to this level becomes smaller and smaller as the bending frequency increases. Both the "down" and the "up" wings extend to higher energy gaps with decreasing bending frequency, i.e., the probability that the collision transfers large portions of energy both to and from the molecule also increases. This means that by decreasing the bend frequency the molecule becomes more active in energy transfer. Similar behavior was observed when the symmetric stretch frequency was varied.

The results presented in Figures 1−4 show that it is probably the bending and to some extent the symmetric stretch mode that participates in the energy transfer. The asymmetric stretch seems to be inactive. A qualitative picture helps to understand why these modes can be the active in the energy transfer from CS_2. The molecule has a linear equilibrium structure. The two atoms at the ends of the molecule are the large and relatively heavy sulfur atoms. The "small" carbon atom is hidden between them. When a collision partner approaches the molecule, the probability that it hits CS_2 along the axis of the molecule is very small. Most of the time the relative velocity of the partners has a component perpendicular to the instantaneous "equilib-

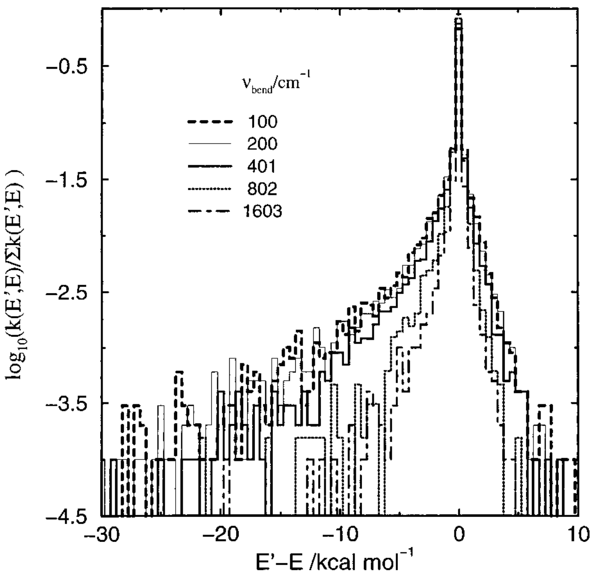

Figure 8. Energy transfer rate coefficients $k(E',E)$ as a function of the energy gap, $E' - E$ at $E = 95$ kcal mol^{-1} at different bending frequencies of CS_2 in a heat bath of 1000 K CO molecules. Continuous line, $\nu_{bend} = 100$ cm^{-1}; long dashed line, $\nu_{bend} = 401$ cm^{-1}; dotted line, $\nu_{bend} = 1603$ cm^{-1}.

rium" axis of the molecule so that the bath molecule can obviously interact with the bend mode. The symmetric stretch mode of CS_2 involves the motion of the two S atoms. To interact with this mode, the collision partner should hit one of the S atoms with a velocity component parallel to the instantaneous molecular axis. This can easily happen as the S atoms are large. The asymmetric stretch mode corresponds to an oscillation of the small and light carbon atom between the two sulfurs. This mode is relatively hard to attack because the carbon atom that should be hit with a velocity component parallel to the molecular axis is hidden and protected by the large end atoms. As a result, due to the geometrical nature of the motions corresponding to the different modes of CS_2, from the point of view of energy transfer the bend mode is the preferred one, the symmetric stretch is expected to have medium activity and the smallest activity can be assigned to the asymmetric stretch mode. This order is identical to the order of frequencies of the modes, and the two factors act in the same direction.

The picture outlined above is in very good accord with the quantum and classical scattering calculations of Clary, Bernshtein, Oref, and Gilbert.[57] They found that in the energy transfer from toluene to rare gas atoms the out-of-plane modes are the most important. Toluene is a basically flat molecule and offers the plane of the molecule for attack with the highest probability. Then, in analogy with the picture sketched above for CS_2, the collider will very probably interact with the out-of-plane modes.

The experimental and the various theoretical observations seem to agree that the lower the frequency of a mode, the more active the mode will be in collisional energy transfer. Our calculations on the variation of the frequency of a given mode as well as the qualitative physical description of how the motion of atoms influences their interaction with the incoming particle, however, point to the existence of a "moderating" effect. The frequency of the mode seems not to be the only factor that determines the activity of the mode: the nature of motion of atoms involved in the given mode determines how large a "cross section" the mode provides for the colliding partner. If the character of the motion of atoms is such that it is "exposed" to larger interaction with the collision partner, the mode will be more active even if the frequency is the same. On the other hand, if the normal mode behavior prevents easy interaction, the mode will be relatively inefficient.

All probability distributions shown in Figure 8. are qualitatively of the same type: on the logarithmic scale $P(E',E)$ descends first approximately linearly with $\Delta E = E' - E$ but has a long tail extending to large ΔE's. This shape has been observed in several systems before.[33−39,55−58] The energy transfer probability as a function of ΔE cannot be described by a single exponential function. The most generally applied form for this purpose is a biexponential function,[16,33,35,38,64,65] (note that Luther et al.[17] recently recommended another function that provides a qualitatively similar shape). The double exponential function has the drawback that the form suggests that there are two kinds of collisions described by the two contributions—a set of "weaker" and a set of "stronger" collisions. No experimental or theoretical facts, however, have been found to support such a distinction. The second exponential is needed only to represent the long tail of the distribution.

When the frequency of an active mode like the bend mode is small, the probability of collisions transferring large portions of energy (named supercollisions[54−57]) increases. The amount of the energy transferred with observable probability also increases in accordance with the widening of the probability distribution. One could think then that the mechanism for supercollisions involves energy transfer through the bend mode. However, when the molecule is "activated" by loosening the bend mode, not only the probability of supercollisions increases but that of all inelastic collisions. It is true that most supercollisions involve energy transfer through the bend mode but the same holds for the "weaker" inelastic collisions, too. In addition, if one "freezes" energy transfer through the bend mode and "activates" the symmetric stretch mode, the shape of the probability distribution as well as the appearance of supercollisions increase in the same way as when the bending frequency is modified. It seems to us that it is very probable that supercollisions do not have a specific common mechanism.

V. Conclusion and Outlook

The model calculations in which we varied the frequencies of the vibrational modes of CS_2 show that in a collinear symmetric triatomic molecule like CS_2 at high vibrational excitation the energy transfer takes place with the participation of the bending and the symmetric stretching modes. The model classical trajectory calculations indicate that for efficient energy transfer the molecule must have low-frequency vibrations. Another factor acting in the same direction is the geometrical nature of the motion corresponding to the bending motion: in most collisions the collision partner will hit the molecule from a direction that will cause an interaction with the bending mode. As a consequence, the activity of the bend mode of CS_2 is due to both factors: the low frequency and the "out-of-line" motion corresponding to the mode.

The observation that the low-frequency modes make the energy transfer more efficient is in very good agreement with the experimental results. The simple theoretical models of an oscillator interacting with a colliding atom worked out in the past (see, e.g., refs 66−70), however, seem not to have focused on the role of the frequency of the relaxing oscillator. The coupling of the vibrational mode to other modes and the occurrence of rotations make the picture even more complicated, so that the field seems to be open for further qualitative models such as the one in refs 51 and 52.

A further factor to be taken into account is that it seems to be generally valid that the frequency of a mode is not the only factor that determines the activity of the mode in energy transfer: the kind of atomic motion corresponding to the given mode also influences the efficiency of the given mode.

Similarly to CS_2, in other polyatomic molecules generally also the frequencies of the bending modes are the lowest. The results of the experiments performed on the collisional energy transfer from molecules with low excitation energy show that in most cases the probability of the energy transfer from these modes is the largest. The explanation in that case is probably similar to that for CS_2: in addition to the low-frequency nature of the mode, geometrical factors can be expected to act in the same direction so that the low-frequency bend modes can be expected to be the most efficient modes in energy transfer. This picture seems to be supported by our calculations that are under way involving energy transfer from nonlinear polyatomic molecules.

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