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Quantum state-resolved, bulk gas energetics: Comparison of theory and experiment

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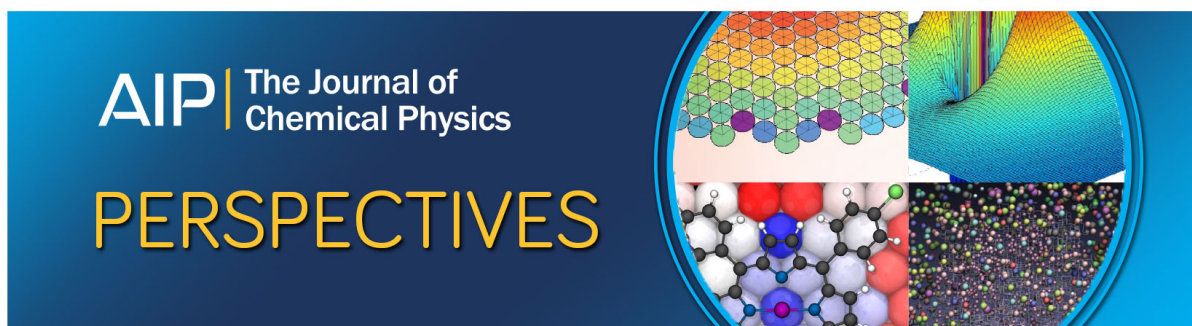
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Quantum state-resolved, bulk gas energetics: Comparison of theory and experiment

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Until very recently, the computational model of state-to-state energy transfer in large gas mixtures, introduced by the author and co-workers, has had little experimental data with which to assess the accuracy of its predictions. In a novel experiment, Alghazi *et al.* [Chem. Phys. **448**, 76 (2015)] followed the equilibration of highly vibrationally excited CsH(D) in baths of H₂(D₂) with simultaneous time- and quantum state-resolution. Modal temperatures of vibration, rotation, and translation for CsH(D) were obtained and presented as a function of pump-probe delay time. Here the data from this study are used as a test of the accuracy of the computational method, and in addition, the consequent changes in bath gas modal temperatures, not obtainable in the experiment, are predicted. Despite large discrepancies between initial CsH(D) vibrational states in the experiment and those available using the computational model, the quality of agreement is sufficient to conclude that the model's predictions constitute at least a very good representation of the overall equilibration that, for some measurements, is very accurate. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4949268>]

INTRODUCTION

In a number of recent publications,¹⁻⁵ the author and co-workers have demonstrated a quantum state-resolved, computational model of collisional-induced energy transfer in gas mixtures consisting of up to 10⁴ diatomic molecules and/or atoms. This approach gives detailed insight into the mechanisms by which energy is exchanged amongst the molecules of an ensemble and is partitioned between the constituent modes and species. Such detailed insight into energy transfer in bulk gases has not been available until quite recently and it represents a field of study still in its infancy. The development of a deeper understanding of energy flow in gas ensembles is of importance in a number of contexts. Systems studied thus far represent small-scale models of processes in planetary atmospheres, plasmas of industrial significance, models of the early universe, and interstellar clouds.⁶ Computational models of energy exchange in such processes can give deeper understanding of large-scale, gas-phase events and hence offer the possibility of enhanced control.

In typical investigations thus far, the equilibration of highly excited diatomic molecules in atomic or molecular bath gases is tracked through a series of collision cycles over many thousands of bimolecular encounters. Quantum state distributions within the rovibrational levels of all constituent species, and modal temperatures, may be sampled at each distinct stage of ensemble evolution. These studies have demonstrated that within a given ensemble, relaxation mechanisms may be quite varied with different inter- or intra-molecular processes dominating at different stages of the ensemble's evolution. The dominant mechanisms depend strongly on the fundamental properties of both excited species

and bath gas; in particular, their energy level structures. A detailed description of the computational model and the collision physics on which it is based is given in a recent publications⁷ and hence is outlined only very briefly below.

The principal aim of molecular collision dynamics investigators over the past 40/50 years has been the accurate determination of single collision rate constants or cross sections⁸ with relatively few studies of the multi-collision environment. Where appropriate data are available,^{9,10} the computational model is in good agreement with single collision experimental findings, and the theoretical method on which the computational routine is based is known to reproduce cross sections for (single) collision-induced vibration-rotation (V-R) transfer data quantitatively.¹¹ By contrast, experimental data on the changes in quantum state populations as a multi-collision ensemble of gases evolves have not been available until very recently as the simultaneous determination of quantum state populations and elapsed time in the microsecond regime represents a difficult task. This situation has changed however following the experimental work of Alghazi, Liu, Dai, and Shen (ALDS).¹² These authors have developed a pump-probe, laser-spectroscopic, technique that achieves simultaneous time discrimination and spectroscopic-resolution. Thus the rovibrational state populations of the initially excited, diatomic molecules may be determined as a function of pump-probe time delay. ALDS follow quantum state population changes in highly vibrationally excited CsH(D) in H₂(D₂) baths as a function of time, and hence as number of collisions increases. The ALDS data therefore have the potential to provide a critical test of the computational approach to energy transfer in bulk gases developed by the author and co-workers.

The computational method is based on the Angular Momentum (AM) theory of collision-induced energy transfer.¹³⁻¹⁷ This formulation, which grew out of experimental

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findings, accurately reproduces a wide range of state-resolved, (single) collision-induced, inelastic, dissociative, and reactive processes,¹⁸ giving new insight into the mechanisms of physical and chemical change. Its basis is the direct calculation of collision-induced linear-to-angular momentum (AM) via a lever-arm (b_n) of molecular dimension. The value of this quantity was determined by experiment to have maximum value (b_n^{\max}) of half bond length of a homonuclear diatomic and the equivalent distances from the centre-of-mass for a heteronuclear diatomic. In computation, a hard ellipsoid surface, known as the Newton surface, in which $A-B =$ half bond length, where A and B are the semi-major and semi-minor ellipsoid dimensions represent the Newton surface. A large number of trajectories impinge on the Newton surface, creating rotational AM and recoil orbital AM at the surface. Each trajectory is subject to strict energy conservation criteria with those not meeting this requirement rejected.

The multi-collision program can deal with up to 10^4 atoms or diatomic molecules and up to three different species. Each diatomic begins in a specified, initial, quantum state and the ensemble is given an initial collision energy or energy distribution. Ensemble evolution is followed over a number, generally at least 1000, collision cycles. In each individual collision cycle, pairs of molecules, chosen at random, undergo binary collisions, after which their new quantum states and velocities are recorded. For an ensemble consisting of 10^4 molecules or atoms, this process is carried out 10^4 times to constitute a single collision cycle. Collision cycles may be repeated at will with the greatest changes occurring over the first few hundred collision cycles. The computation is generally continued to at least 1000 and generally to 2000, cycles. The collision cycles may be individual or groups of cycles, following which the quantum state populations in each species are ascertained, as are the modal temperatures of vibration, (T_v) rotation (T_r), and translation (T_t). Note that the quantum state populations represent the primary data available from the computation. However, the variation of modal temperatures, plotted as a function of number of collision cycles, gives a very useful overview of the energy exchange processes. It should also be noted that the identification of the initial, singly occupied, state with a definite temperature, rather than as a well-defined energy, is of course, a fiction, and in this and related work, is used for convenience of result presentation only. Representation of state populations in terms of modal temperatures becomes more realistic as the ensemble evolves. As implied above, the modal temperature plot is simply a useful means of compressing a very large amount of data into a form that will be familiar to workers in the field of gas kinetics and dynamics. A more detailed description of the method including a discussion of computational errors, etc. is given in a recent publication.⁷

Here the ensemble computational method is used to investigate the relaxation of vibrationally excited CsH($v;j$), present as the 1:10 ratio, minor component of a binary gas mixture in which the majority- or bath-species is H_2 . In addition, ALDS follow the equilibration of highly excited CsD($v;j$) in D_2 and comparison between experiment and the predictions from the computational model in these two ensemble systems forms an important part of the

evaluation process. However, although theory and experiment are compared for the same ensembles and species as those investigated by ALDS, the initially populated alkali hydrides (deuterides) differ very considerably in their level of excitation. ALDS obtain data on the equilibration of alkali hydrides populated in vibrational states $v > 20$. Quantum levels at this degree of excitation exceed the capacity within the computational model, which is currently limited to $v \leq 10$. Despite this, reasonably close similarities between experiment and computer model predictions are to be expected as earlier work has demonstrated¹⁹ that the identities of target and bath molecules are the principal determinants of the outcome of the equilibration process.

In this study, the search is for similarities in, for example, de-excitation mechanisms, modal temperature evolution, and decay rates for the CsH(D) component. In the ALDS experiment, quantum state population data from the alkali hydride (deuteride) are obtained as a function of pump-probe time delay, whereas in the computational plots, changes in quantum state populations and modal temperatures are calculated as a function of number of collision cycles. For the purposes of comparison, the latter are converted to a time coordinate using the experimental gas pressure data published by ALDS. The calculated relation between the two is that $80 \mu s \approx 1600$ collision cycles.

RESULTS

T_v of CsH($v;j$) in H_2 500 K

ALDS¹² report plots of modal temperature (T_m) as a function of pump-probe time delay for CsH ($v;j$) = (21;10) in $H_2(0;j)$ at 500 K and also studied ensembles of CsH($v;j$) in H_2 for $v \geq 16$ in greater detail, using their time-resolved, high resolution spectroscopic method. This work confirmed the existence of what have been termed²⁰⁻²³ multi-quantum (MQ) and sequential, single-quantum (SQ) mechanisms of energy transfer in this and related systems. The former process consists of direct population transfer between vibration states, often over many vibrational quanta, within a target molecule, CsH in this case. These transitions are assumed to accompany population gain of, in general, a single, vibrational quantum, within the H_2 bath gas. The MQ process represents an ultra-fast energy exchange, particularly when the combination of energy loss by the excited species, and gain by the bath, has small energy defect.¹⁻⁵ The SQ mechanism on the other hand consists primarily of vibration-rotation (V-R) transfer within the CsH molecule and results in a slower deactivation. Though now an established descriptor, the expression “sequential single quantum-state” is not a wholly accurate representation of the processes involved in vibration-rotation transfer. Rotational transfer within a vibrational manifold often results in change by many Δj quanta, although the probability of such change falls with the magnitude of Δj , and as a result, there is a bias towards low Δj transitions. In addition, for these highly excited states, there is likely to be extensive inter-vibrational manifold transfer involving rotational state change in which there is little energy change—the well-established quasi-resonant, vibration-rotation transfer

(QVRT) mechanism.^{24–27} In what follows, reference to the SQ mechanism will be assumed to include any or all of the rotational relaxation mechanisms, i.e., pure rotational state transfer as well as processes that change vibration- and rotation-states simultaneously each of which may involve multi-quantum, rotational state transfer.

The MQ and SQ terminology for intra-molecular events in the processes of equilibration was introduced by Wodtke and co-workers^{20–23} who demonstrated the existence of fast decay routes from excited O₂, NO, and other diatomics, involving loss of many vibrational quanta from the initially excited state. Parmenter and co-workers also reported multi-quantum vibration state exchange both in diatomic molecules and in excited polyatomics.^{28,29} The existence of MQ and SQ processes in excited diatomic molecules in diatomic bath gases has also been demonstrated by the author and co-workers in a range of gas mixtures,^{1–7,30} using the computational method to follow gas ensemble equilibration. The principal emphasis in the current study is on the comparison between the time- and quantum state-resolved data reported by ALDS and predictions obtained using the computational/theoretical model developed by the author and co-workers^{13–17} as a means of validating the latter.

The principal experimental findings of ALDS of relevance to this work are summarised as follows:

- (i) Analysis of rate constant data at different stages of ensemble evolution indicates that energy transfer processes generally are multi-staged with different transfer rates characterising each different stage. These different stages are indications of changes in the dominant mechanism, some being fast and some slow.
- (ii) For CsH ($v_i \geq 16$), where v_i denotes initial vibrational state, the early stages of ensemble evolution consist primarily of fast, near-resonant, vibration-vibration (V-V) MQ energy transfer within CsH with $\Delta v = -8$.
- (iii) Plots of CsH vibrational temperature, (T_v), as a function of pump-probe delay indicate three distinct regions of energy exchange. On closer analysis, the initial phase was found to be dominated by fast, V-V transfer within CsH. No monitoring of state populations within the H₂ bath gas was carried out, but energy conservation requires simultaneous $\Delta v = +1$ excitation in H₂ molecules of the bath gas. This combined CsH–H₂ energy transfer process has a small overall energy defect that is readily made up by rotation state change. The second phase is slower and consists of single quantum (SQ) vibration-rotation relaxation. This is followed by the third phase in which little change occurs as the system follows slow pathways to equilibration. These findings mirror those reported by Wodtke *et al.* on vibrationally excited O₂ and NO.^{20–23}
- (iv) The experimental cross section for the initial, MQ fall of T_v was calculated to be $4.6 \pm 1.1 \text{ \AA}^2$.

Several of the principal conclusions drawn by ALDS in their analysis of the CsH(D) data are similar to those deduced by the author and co-workers using the computational approach to gas phase, multi-collision energy transfer.^{1–7} In order to evaluate the quality of the computational predictions, experimental data from figures reported by ALDS¹² have

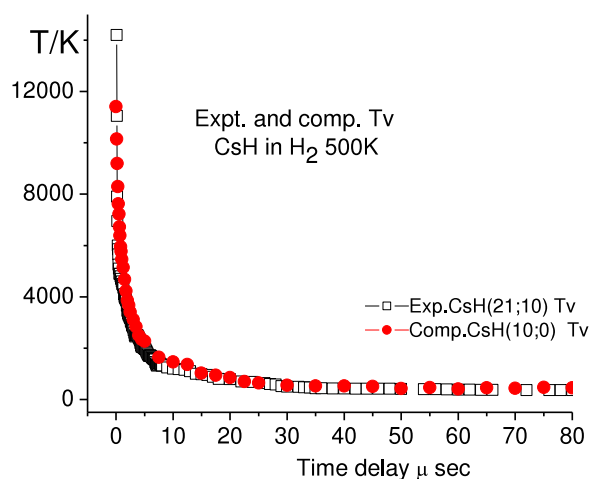


FIG. 1. Experimental (black squares) and computed (red circles) values of vibrational temperature (T_v) as determined by experiment for CsH(21;10) in H₂ at 500 K and computationally for CsH(10;0) in H₂, also at 500 K. The T_v are plotted as a function of pump-probe delay in μs .

been taken from published graphs for direct comparison with the corresponding computer predictions. Fig. 1 displays the experimental decay curve (filled red circles) of T_v for CsH(21;10) in H₂ (Fig. 19 of that publication). Superimposed on this (open black squares) are the computed T_v for CsH(10;0). Both data sets were determined at a collision energy = 500 K. The striking feature of this figure is the agreement between experiment and computed decay curves. Note however that an element of good fortune may play a part here. The CsH initial states in the two sets of data vary by an energy difference equivalent to 11 vibrational quanta. However, the point was made earlier, emphasised by ALDS, that for a given ensemble, the shape of the T_v versus time delay plot is determined by the dominant relaxation mechanisms. Thus the close similarity in the two decay curves of Fig. 1 is likely to reflect very similar relaxation mechanisms, despite the different starting points for the initial excitation.

The three-stage structure of vibrational relaxation in the CsH in H₂ system, referred to above, is less clearly evident in Fig. 1 than in, for example, CsD in D₂ which is discussed in more detail below. The cross section for collision-induced energy transfer from CsH(10;0) in H₂ is readily calculated from the loss of population from the initially populated CsH state resulting from the first complete collision cycle. These data are available from the program. As each single collision cycle consists of a unique, random selection of partners for collision, the first collision cycle was repeated 20 times and the mean value of population loss from CsH($v = 10$) calculated. On conversion to collision cross section, this was found, at $2.8 \pm 0.2 \text{ \AA}^2$, to be close to the experimental value of $4.6 \pm 1.1 \text{ \AA}^2$ determined by ALDS for CsH (21;10) in H₂.

Near-resonant V-V transfer: CsD in D₂

Pathways by which CsD($v;j$) deactivates in D₂ in the low energy, harmonic region of the CsD potential energy curve are clearly seen in Fig. 2. In this figure, vibrational state populations are plotted in a form that quantifies the changes as number of collision cycles increases. Fig. 2 demonstrates

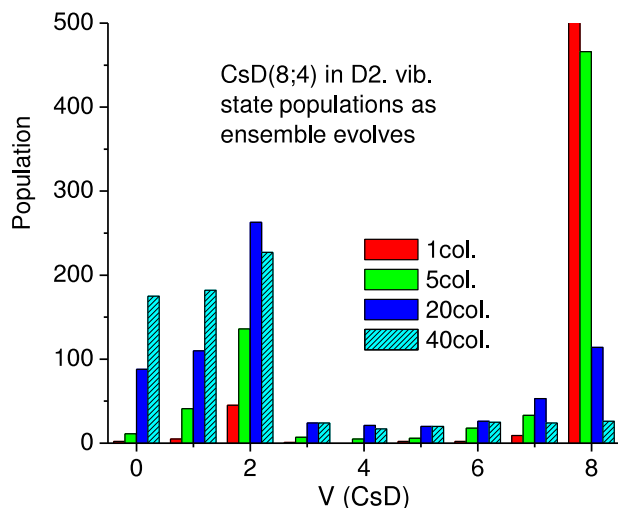


FIG. 2. Evolution of CsD vibrational state distributions as a function of number of collision cycles. For $v = 8$, the initially populated state of CsD, population extends off-scale in the figure but has fallen to ~ 100 after just 20 collision cycles.

clearly that the dominant, initial, equilibration process for CsD (8;4) in D₂ in this region is fast, multi-quantum ($\Delta v = -6$) V-V transfer from initial CsD $v = 8$, a process that begins with the first collision cycle. This differs from the $\Delta v = -8$ near-resonant V-V processes observed by ALDS in the CsD high-energy, anharmonic region. It is likely that the mechanisms inherently are very similar. The $\Delta v = -8$ transition in CsH (21;10) is near-resonant with $\Delta v = +1$ from the ground state of H₂ bath gas as is the $\Delta v = -6$ exchange in CsD(8;4). Energy transfer to the bath gas, which is monitored simultaneously in the computation, is discussed in more detail below. Fig. 2 demonstrates that fast, MQ transfer within CsD accounts for the very rapid fall in T over the first few μs seen in Fig. 1. Following ~ 15 -20 collision cycles ($\sim 1 \mu\text{s}$), $v = 2$ has become the most populated vibrational state, and from this point, vibration-rotation transfer has become the principal relaxation mechanism. Near-resonant, MQ, V-V transfer is not possible from CsD v -states lower in energy than $v = 6$ as the energy released is insufficient to excite D₂ bath molecules to their first vibrational state.

T_m of CsD(v;j) in D₂: Theory and experiment compared

Fig. 3 plots the experimentally determined evolution of modal temperatures of vibration, (T_v) rotation (T_r), and translation (T_t) for CsD(27;10) in a bath of D₂ molecules at 500 K. This was re-drawn, using data taken from Fig. 23 of ALDS.¹² The three distinct phases of vibrational energy loss from CsD are now clearly apparent in the T_v plot. However, it is evident that in the initial phase, T_v for CsD (27;10) in D₂ falls more slowly than was found for CsH(21;10) shown in Fig. 1. ALDS interpret this as indicating the suppression of the fast V-V mechanism and greater reliance on slower, vibration-rotation interconversion processes for energy reduction. ALDS studied CsD ($v > 20$) in D₂, finding clear evidence of near-resonant V-V transfer in which $\Delta v = -8$. The slow fall of T_v in Fig. 3 suggests that the pathway by which deactivation occurs is also a function of the initially

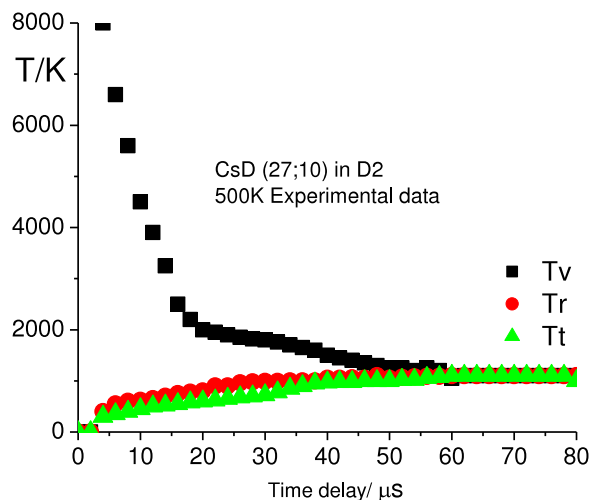


FIG. 3. Evolution of the modal temperatures of vibration (T_v), rotation (T_r), and translation (T_t) for CsD(27;10) in a bath of D₂(0;0) at 500 K plotted as a function of pump-probe delay time in μs . Data taken from Fig. 19 of ALDS.

populated state, as found by Wodtke *et al.*²⁰⁻²² Like-for-like comparison with the deactivation of the very highly excited caesium hydrides investigated by ALDS was not feasible for reasons discussed earlier. However, it is of interest to compare the data of Fig. 3 with the evolution of modal temperatures for CsD(10;0) in D₂(0;0) as previous studies of ensemble behaviour^{1,19,30} suggest that the chemical identity of the molecules involved is a significant determinant of the relaxation mechanisms within a given gas ensemble. A number of identifiable common features therefore might be anticipated. Despite a difference of some 17 vibrational quanta between initially excited CsD(10;0) in the computation and CsD(27;10) in the experiment, Fig. 4 demonstrates that there is a reasonable degree of agreement between experiment and the computer prediction in overall shape of CsD T_m plots as a function of pump-probe delay. The principal difference between experiment and theory lies in the speed of deactivation

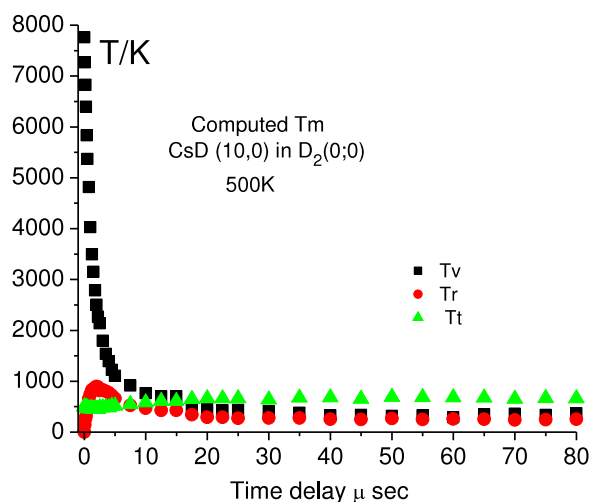


FIG. 4. Computed prediction of modal temperatures of vibration (T_v), rotation (T_r), and translation (T_t) for CsD(10;0) in a bath of D₂(0;0) at 500 K plotted as a function of pump-probe delay time in μs .

of T_v , which, in the initial phase, is computer-predicted to be faster than that observed experimentally in CsD(27;10). This may partly result from imprecision in the data that initially are computed as a function of number of collision cycles and converted to pump-probe delay time using the ALDS experimental conditions. This conversion is sensitive to experimental gas pressure stated by ALDS to be “about 3 Torr.” A relatively small variation in the collision cycles–delay time conversion factor would result in a computed T_v decay curve closely similar to that obtained from experiment with little effect on T_r and T_t .

ALDS attribute the differences in T_v relaxation behaviour between CsD(27;10) in D_2 (Fig. 3) and CsH(21;10) in H_2 (Fig. 1) to suppression of fast V-V transfer at one or more points in the energy loss chain in the case of the former. Thus there remain a number of unsolved queries regarding the relaxation of highly excited diatomics from this and earlier work. Wodtke and other workers^{20–23} pointed to instances in the equilibration of highly vibrationally excited O_2 in which near-resonant V-V is *not* observed, despite what appear to be suitable conditions for this mechanism to operate. A study has begun of the vibration-rotation relaxation mechanism in systems for which near-resonant V-V transfer is precluded. Thus for CsD(4;j) in D_2 (0;0), insufficient energy is released in the $\Delta v = -4$ transition in CsD to excite $v = 1$ in the D_2 bath molecules. Preliminary results suggest that this relaxation, presumed to constitute SQ processes alone, occurs somewhat more slowly than is seen in CsD(10;0) in D_2 (Fig. 4) where fast V-V dominates, though not as slowly as for CsD(27;10) in D_2 (Fig. 3). A more detailed study on the nature of the SQ mechanism, in particular the role of molecular rotations and angular momentum conservation, aspects that in general have not featured in the analyses of experimental data, will follow this work.

An interesting difference between experiment and theory is seen in the very earliest phase of equilibration as a small, but quite distinct, peak in T_r that is present in the computational calculation but not seen in experiment. The peak is reached very rapidly, after which it decays slowly, eventually equilibrating to a temperature slightly lower than that of T_t . As discussed earlier, in the computation, the evolution of energy transfer among the modes is determined as a function of number of collision cycles. In an ensemble containing 10^4 molecules, a single collision cycle consists of 10^4 binary collisions between pairs of molecules chosen at random. In the transformation from collision cycles to pump-probe time delay, 1 μ s corresponds to ~ 20 such collision cycles at the gas pressures reported by ALDS. Thus it is possible to identify processes computationally in the earliest part of ensemble evolution before the photon counting of probe fluorescence is able to begin.

That a change in rotational state populations accompanies vibrational state change is not surprising. The initial V-V exchange will generally not be precisely energy resonant with the $0 \rightarrow 1$ vibration state change in H_2 and so rotational state change would be needed to ensure energy conservation in the combined CsD de-excitation– D_2 excitation. Furthermore, on collision between the diatomics, orbital angular momentum is generated, which is then partitioned between molecular

rotation and recoil in a manner that conserves total angular momentum. In common with other computational data obtained on the overall evolution of the ensemble from disequilibrium to equilibrium in a wide range of molecular ensembles,^{1,19,30} the computed T_m do not converge to a common temperature over the collision, unlike those from experiment (Fig. 3), which do so within $\sim 60 \mu$ s or ~ 1200 collision cycles. The discrepancies are relatively small with ~ 100 K difference between “equilibrated” T_v and T_r , with $T_t \sim 250$ K higher. All are close to the bath temperature of 500 K. The computational model reproduces the experimentally determined T_m versus pump-probe time delay curves in a form quite close to those determined by experiment. In addition, the principal V-V process is matched accurately for T_v in CsH with the collision cross sections for initial vibrational decay very close in magnitude to that found by experiment. Recent work has demonstrated³¹ that within gas ensembles containing diatomic molecules, there is competition for available bath angular momentum between molecular rotation and angular momentum of recoil. In this, molecules of low reduced mass fare badly and T_r for these species is invariably lower than T_t . This is evident for CsD in D_2 (Fig. 4) in which T_r is ~ 420 K less than T_t . This effect, which is the result of energy constraints on the linear-to-angular momentum conversion process, reduces the available range of the effective impact parameter (b_n).³¹

Energy transfer to the bath gas

The foregoing discussion has concerned the pathways by which initial excess energy within the CsH(D) minor component equilibrates with its $H_2(D_2)$ surroundings. In many circumstances, processes in Earth’s atmosphere, for example, the extent of energy transfer into the molecules of the bath gas and its ultimate destination, may be of greater interest. The computational model is able to follow state-to-state energy transfer within molecular ensembles consisting of up to three constituent species and it is of interest to examine how the bath gas responds to the population shifts within the guest molecules. Figs. 5 and 6 give an overview of energy

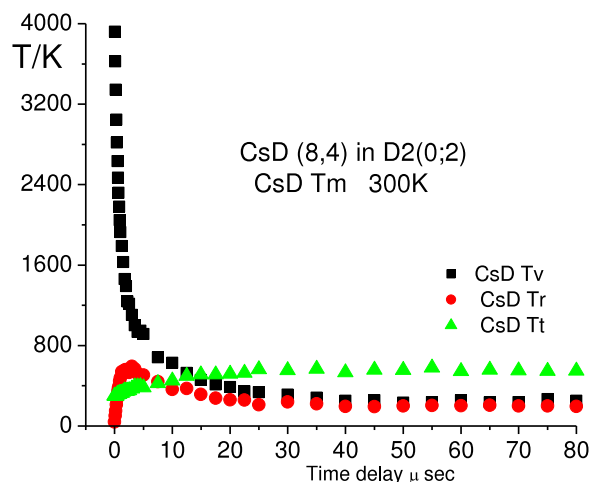


FIG. 5. Evolution of modal temperatures of CsD (8;4) in a bath of D_2 molecules at 300 K as a function of pump-probe time delay.

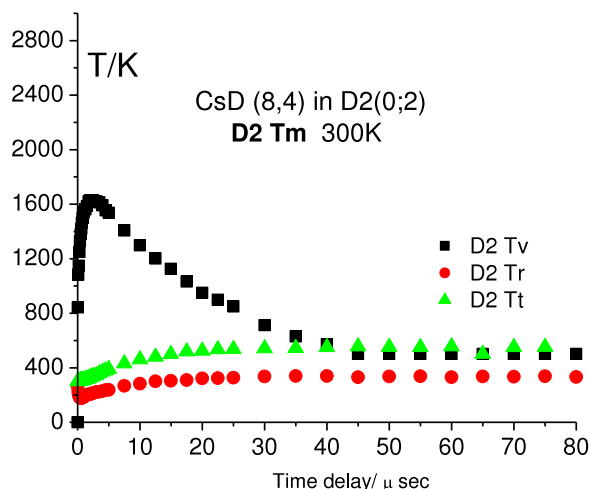


FIG. 6. Evolution of modal temperatures as a function of pump-probe time delay for D_2 in a 1:10 ratio mixture of $CsD(8;4)$ in a bath of $D_2(0;2)$ molecules at 300 K.

redistribution from $CsD(8;4)$ both to other rovibrational states within CsD (Fig. 5) and the D_2 bath gas Fig. 6. These two figures illustrate the exchange and transfer of rotational energy from the outset of ensemble evolution. The fast, initial, vibrational energy loss in CsD through $v = 8 \rightarrow v = 2$ V-V transfer is balanced by rapid vibrational heating of the D_2 bath gas. At the same time, the rise of T_r in CsD in the very earliest phase is matched by a fall in rotational temperature within D_2 . Following this turbulent initial phase, T_v for D_2 follows a slow exponential decay, eventually equilibrating with the translational temperature at a slightly higher value than T_r .

CONCLUSIONS

The computational model of state-to-state energy transfer in large gas ensembles, developed by the author and co-workers, has been used to track the dispersal of excess energy in gas ensembles consisting of highly vibrationally excited CsH in H_2 and CsD in D_2 at 500 K. Recent experiments by Alghazi *et al.*¹² on these multi-collisional ensembles incorporate both spectroscopic- and time-resolution, allowing the modal temperatures of vibration, rotation, and translation to be determined as a function of pump-probe time delay on the μs time scale. These results provide a test of the computational model and its ability to reproduce the experimental data obtained on caesium hydrides. However, like-for-like comparison is not yet a possibility as the experimental data were obtained on Cs hydrides that initially are excited to very high vibrational states ($v > 20$), a degree of excitation that is beyond the current capacity of the computational model. Despite this, key features are expected to be reproduced, as previous experience suggests that much of the relaxation process is determined by the fundamental properties of the molecules involved, particularly the energy level structure of their rovibrational quantum states. The computational model accurately reproduces the early dominance of fast, $\Delta v = -6$, multi-quantum V-V mechanism both qualitatively, and with good agreement

between experimental and computed cross sections. There is also quantitative agreement between the computed T_v decay curve for $CsH(10;0)$ in H_2 and the experimentally determined T_v for $CsH(21;10)$ in H_2 .

Analysis of $CsD(8;4)$ in D_2 vibrational distributions as a function of the number of collision cycles demonstrates that $CsD v = 8 \rightarrow v = 2$ transfer begins from the first collision cycle and that following ~ 40 collision cycles, much of the initial CsD population has migrated to $v \leq 2$. This agrees with related findings of ALDS. When the deactivation of $CsD(27;10)$ in D_2 is compared to the model's predictions based on $CsD(10;0)$ in D_2 , it was found that the computed T_v falls faster than that observed experimentally. Further, there is an early peak in T_r that is predicted computationally but is not seen by ALDS. This latter observation may not represent a disagreement with experiment as the T_r peak rises and then falls within the first few μs , a difficult region for the experiment. The model's agreement with the $CsD(27;10)$ data is less good than anticipated though, as mentioned earlier, in no instance was it feasible to compare theory with experiment on $CsH(D)$ systems with the same degree of initial excitation.

The bath gas data are of interest as a substantial fraction of the initial vibrational energy is deposited into quantum states of the H_2 or D_2 bath molecules. The data show that T_v of D_2 rises very rapidly for the duration of the fast V-V transfer and then slowly equilibrates. Furthermore there is a dip in T_r of D_2 that coincides with the aforementioned peak seen in CsD rotational temperature. Thus although it has not been possible to compare exact like with like, the similarity between the evolution of the T_m predicted by the computational model and that obtained from experiment establishes that the computational method and its underlying mechanics provide *at least* a good first approximation to state-to-state energy transfer in large gas ensembles containing diatomic molecules, a small fraction of which are far from equilibrium. A typical computational run will incorporate some 10^7 individual, binary, diatom-diatom collisions, and the agreement with experimental data found here suggests that the error per binary collision is small.

Predicting the pathways of energy transfer in large gas mixtures represents a field of some significance in environmental and industrial contexts. As stressed in earlier work, the capacity to follow state-to-state energy transfer in large gas volumes represents the principal departure from earlier methods of treating the energetics of large gas volumes and takes this field beyond the constraints inherent in the assumption of local thermodynamic equilibrium.

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