POSSIBLE QUANTUM EFFECTS IN COLLISIONAL ENERGY TRANSFER IN HIGHLY EXCITED MOLECULES

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Received 10 October 1989; in final form 24 January 1990

It has been observed that classical trajectory calculations of energy transfer rates in large highly excited molecules with He bath gas give values much higher than experiment. This might be caused by quantum effects in which contributions from higher partial waves do not contribute to energy transfer. Experimental means of testing this postulate are proposed.

1. Introduction

Interpreting and predicting rate coefficients for unimolecular and recombination reactions in the fall-off regime require a knowledge of the rate $R(E, E')$ of energy transfer of a highly excited ("substrate") molecule with internal energy E' to energy E, by collision with a bath gas M. Efficient means of deducing this quantity (or its lower moments, which are sufficient to predict most data of interest) from classical trajectories have recently been deduced [1]. Extensive calculations have been carried out [2] with this method for excited azulene/rare gas collisions, for which there are extensive experimental results [3,4]. Other classical calculations, using somewhat different techniques, have been carried out with CS_2 as substrate [5]. These calculations employed potential functions of the type that are frequently assumed to be reasonable for such systems: a valence force field for the substrate and atom/atom Lennard-Jones or exp–6 for the rare gas/substrate interactions. The calculations were shown to be properly converged, i.e. they represented an accurate evaluation of the classical energy transfer rate.

For heavier bath gases, the azulene trajectory calculations gave results that were in accord with experiment. However, this was not the case for the lightest bath gases: for example, the root-mean-square energy transfer per collision for He was found to be about a factor of 3 greater than that deduced from experiment.

This discrepancy is most likely to arise from one (or both) of two obvious causes: (1) the potential function employed was inaccurate, and/or (2) quantum effects are significant (for a review of earlier work on quantum effects, see Hippler and Troe [6]). There are a number of ways that this problem could be resolved:

(a) The first would be to obtain an accurate bath gas/reactant potential (e.g. by quantum calculations or from spectroscopy of van der Waals molecules) and compare it with that used in the trajectory calculations. Indeed, comparison with the trajectory results from a Lennard-Jones 12–6 and an exp–6 interaction indicate that the softer (exp–6) repulsive wall will bring the trajectory results more in accord with experiment. However, these results also suggested that accurate agreement could only be obtained for He bath gas by making the repulsive wall much softer than would be expected. While the form of the interaction potential is still an open question, it is still proper to search for alternative explanations.

(b) The question concerning the importance of quantum effects could be answered by carrying out an accurate quantum mechanical evaluation of the energy transfer rate and comparing it with the classical result for the same interaction potential. However, even a classical evaluation of this rate for a typical system, such as azulene/rare gas energy transfer, is still a major computational undertaking, and accurate quantum mechanical computations for large, highly excited, polyatomics are impossible for the immediate future. We note, however, that it may be possible to carry out moderately accurate estimates of quantum effects through methods such as the Gaussian wavepacket technique [7] (the only quantum calculations of reasonable accuracy for large polyatomics are those of Clary [8] for *p*-difluorobenzene, but here the substrate energy was comparatively low).

(c) The question of the importance of quantum effects could be resolved by appropriate experimental data. We shall return to this point.

In this note, we suggest how the differences between the classical trajectory results and experiment with He bath gas could be ascribed to the inadequacies of a classical treatment of the dynamics. We also propose a straightforward experimental means of ascertaining the correctness of our suggestion.

It is well known that classical total elastic cross sections are infinite, whereas the quantum equivalents are finite [9]. Thus, contributions from higher impact parameters, corresponding to higher partial waves, make smaller contributions to the energy transfer rate than those calculated in a classical evaluation. It will be seen that there is a particularly large contribution to the energy transfer rate from a "rim" of trajectories with impact parameters near the Lennard-Jones radius. This could lead to a large reduction in the quantum energy transfer rate, compared to the classical one, for the lightest bath gases, such as He, where quantum effects might be most important.

2. Possible quantum mechanical origins of the discrepancy

We first summarize, in eqs. (1)–(4), the classical mechanical expression for the average energy transfer rate, $R(E, E')$, and its moments. The fundamental classical expression for $R(E, E')$ is given by [1]

$$R(E,E')=\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\int_0^\infty 2\pi b\,\mathrm{d}b\int_0^\infty \mathrm{d}E_r\,\frac{E_r}{(k_BT)^2}\times\exp(-E_r/k_BT)\,\hat{B}(E,E',E_r,b)\,, \tag{1}$$

where $\hat{B}$ is the probability of a classical trajectory with impact parameter b, initial internal energy E', and initial translational energy E_r, finishing with final internal energy E, and μ is the reduced mass of the reactant/bath gas pair. The rate coefficient of a unimolecular or recombination reaction, and the results of so-called "direct" measurements of the energy transfer rate [3,4], are not sensitive to the full functional form of $R(E, E')$ but rather to only a single moment. For computational purposes, the most convenient of these is the second moment, $R_{E',2}$:

$$R_{E',2}=\int_0^\infty (E-E')^2R(E,E')\,\mathrm{d}E\,. \tag{2}$$

The classical expression for $R_{E',2}$ is given by [1]

$$R_{E',2}=\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\int_0^\infty 2\pi b\mathrm{d}b\int_0^\infty \mathrm{d}E\,(E-E')^2\times\int_0^\infty \mathrm{d}E_r\,\frac{E_r}{(k_BT)^2}\exp(-E_r/k_BT)\,\hat{B}(E,E',E_r,b)\equiv\int_0^\infty I(b)\,\mathrm{d}b\,. \tag{3}$$

The evaluation of this moment is through classical trajectories, where the integrand is evaluated with the usual Monte Carlo selection of initial conditions. This is written explicitly as [1]

$$R_{E',2}=\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\lim_{N\to\infty}\lim_{b_{\max}\to\infty}\pi b_{\max}^2\frac{1}{N}\sum_{j=1}^{N}(\Delta E_j)^2\,, \tag{4}$$

where N is the number of trajectories, $b_{\max}$ is the maximum impact parameter chosen, and ΔE_j is the energy change in the *j*th trajectory.

We now examine the contributions of various impact parameters to $R_{E',2}$: that is, by examining the dependence of the integrand $I(b)$ of eq. (3) on the impact parameter *b*. This is shown in fig. 1 for azulene/He trajectories, obtained using data reported by Lim and Gilbert [2], and for CH_3O_2/Ar in fig. 2, using data reported by Whyte and Gilbert [10].

It is apparent from figs. 1 and 2 that the largest contribution to eq. (3) comes from impact parameters that are slightly smaller than what one might term the "Lennard-Jones" radius $\sigma[\Omega^{2,2*}]^{1/2}$, where σ is the Lennard-Jones distance parameter for the spherically averaged bath gas/reactant interaction potential and $\Omega^{2,2*}$ the dimensionless collision integral [11]. This supports the common practice [12] of assuming that the total collision rate for energy transfer, *Z*, is given by

$$Z=(8k_BT/\pi\mu)^{1/2}\pi\sigma^2\Omega^{2,2*}\,. \qquad (5)$$

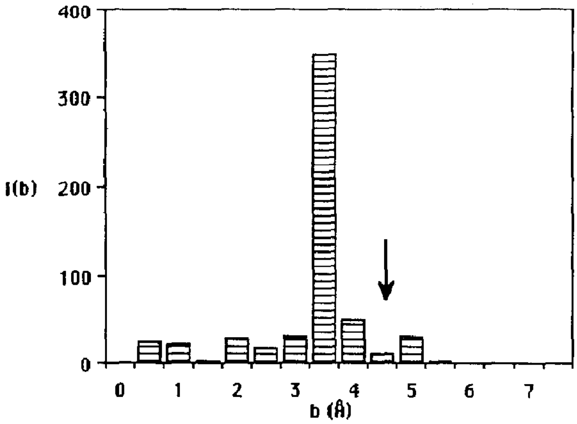

Fig. 1. Contributions to overall energy transfer rate from each range of impact parameter $I(b)$ of eq. (3), from trajectory data of Lim and Gilbert [2] for He/azulene collisions at 300 K with initial azulene internal energy $E'=17500\ \text{cm}^{-1}$. Arrow denotes Lennard-Jones radius $\sigma[\Omega^{2,2*}]^{1/2}$.

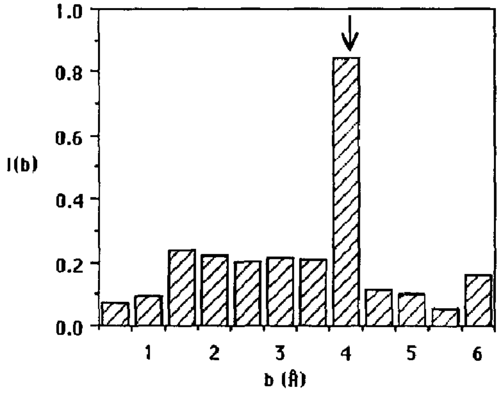

Fig. 2. Contributions to overall energy transfer rate from each range of impact parameter $I(b)$ of eq. (3), from trajectory data of Whyte and Gilbert [7] for Ar/CH_3O_2 collisions at 440 K with initial azulene internal energy $E'=10^4\ \text{cm}^{-1}$. Arrow denotes Lennard-Jones radius $\sigma[\Omega^{2,2*}]^{1/2}$.

Presaging the development given later in this note, it is essential to point out that there is *no* rigid justification for using eq. (5) to define a total collision rate. Eq. (5) is usually evaluated classically, yet the true classical value of $Z=\int R(E, E')\,\mathrm{d}E$ is often *infinite*, because of the well-known "elastic peak" arising from contributions from large impact parameters for small $|E-E'|$ [13]. The use of eq. (5) is semiempirical. It may be justified by noting that the classical expression for the gas viscosity also has the hard-sphere expression modified by the term $\Omega^{2,2*}$, and that this classical viscosity expression usually gives good accord with experiment (except for obvious quantum effects such as in He at low temperatures). Moreover, by rationalizing that viscosity is average momentum transfer for *elastic* scattering, it is likely that an average total energy transfer rate for *inelastic* scattering would be given by the same expression, to a good approximation.

At this juncture we note that it is common, although not necessary, for an a priori calculation (as described from classical trajectories in eqs. (1)–(4)) to factor $R(E, E')$ or its moments into a collision rate *Z* and a probability of energy transfer per collision, $P(E, E')$:

$$R(E,E')=ZP(E,E')\,. \qquad (6)$$

Similarly, we have the relation $R_{E',n}=Z\langle\Delta E^n\rangle$ between the moments $R_{E',n}$ and $\langle\Delta E^n\rangle$ of $R(E, E')$ and $P(E, E')$. These relations have no fundamental physical meaning but are necessary for *approximate* developments in which we wish to obtain simple models for $R(E, E')$ by developing separate approximate models for *Z* and for $P(E, E')$.

We now examine the sort of *qualitative* changes that might be brought about by a quantum mechanical treatment of $R(E, E')$. The most important difference between classical and quantum *elastic* rates is that the latter are finite while the former are infinite (for potentials that are not identically zero beyond a given distance). The classical divergence is because there are non-zero deflections for arbitrarily large impact parameters, corresponding to small deflection angles $\Theta(b)$. On the other hand, the quantum mechanical result is finite because of interference between the two regions of partial waves (corresponding classically to the impact parameters) where $\Theta(b)=0$: those as $b\rightarrow\infty$ and those where $\Theta(b)\approx 0$ at a finite impact parameter [14].

While the foregoing arguments apply only to elastic scattering in a spherically symmetric potential, they suggest that similar considerations may be semi-quantitatively applicable to the case of inelastic scattering, in the following way. The interference between matter waves that annuls the classical elastic divergence suggests that higher partial waves (impact parameters) may have a contribution to the inelastic scattering that is less than predicted from a straightforward classical calculation, as in eq. (3). The impact parameters for which this diminution is likely to occur are those close to (and beyond) where $\Theta(b)=0$. For the data shown in fig. 1, this can be estimated from the initial translational energy (E_t) and the $\Theta(b)$ for the spherically averaged Lennard-Jones potential parameters for this system. The data of Lim and Gilbert [1] give $E_t\approx 2k_BT$ ($T\approx 300$ K), $\sigma=4.6$ Å and $\epsilon=72$ K. We then find $\Theta(b)=0$ for $b/\sigma=1$, i.e. $b=4.6$ Å. It is apparent from fig. 1 that there are large contributions to the energy transfer rate from impact parameters only slightly less than this value. This strongly suggests that the calculated energy transfer rate could be significantly reduced if the contributions to $R_{E',2}$ were omitted from impact parameters close to this value of b. This could readily explain the discrepancy between the values calculated from trajectories and experiment.

It is essential to realize that the suggested quantum effect cannot be ascribed to a simple separation of $R(E, E')$ into Z and $P(E, E')$ and then saying that quantum effects make the assumed Z too large. It is re-emphasized that this separation is artifactual, and the comparison between experiment and theory discussed here completely obviates any such separation (even though for conceptual convenience one reports results as mean energy transferred "per collision"). The suggested quantum effect is in the classical rate, and there is no need for any artifactual (although convenient) separation into a "Z quantum effect" and a "$\langle\Delta E\rangle$ quantum effect".

An apparent argument against the quantum effect as suggested above is that the classical and quantum mechanical values of $\Omega^{2,2*}$ for the above conditions differ by less than 1% [11]. However, it should be recalled that there is no a priori reason that $\Omega^{2,2*}$ should be directly related to the magnitude of the average energy transfer rate. As stated, it is found that $\Omega^{2,2*}$ does reflect the maximum impact parameter contributing to $R_{E',2}$, but has nothing else to say about the b dependence of the integrand $I(b)$ which determines $R_{E',2}$.

Another possible quantum mechanical origin of the discrepancy is the effect of zero-point energy [15]. The density of states of the substrate (azulene) at the internal energy in question is extremely high, and these states are strongly mixed by anharmonicity both in the isolated reactant and from the interactions with the bath gas during the collision. Moreover, if the discrepancy between trajectory and experimental results arose from not accounting for azulene zero-point energy, then the discrepancy would be observed for both light and heavy bath gases (which of course do not affect the reactant zero-point energy); such however is not the case. Thus, at first sight it would appear that there should be no "intramolecular" origin for quantum effects (as distinct from the "intermolecular" effect suggested above). However, the total energy of the substrate is such that the average excitation per oscillator is about one quantum. It is, therefore, conceivable that some quantum effects arising from the zero-point energy in each mode could reduce the energy transfer rate.

Yet another possible quantum effect is that involved in the "propensity rules" seen to influence collisional energy transfer of large molecules at moderately low internal energies [16]. However, for large, highly excited polyatomics (as in the azulene/He system which is our principal concern here) the huge density of states, together with the fact that IVR in such systems occurs on about the timescale of a collision (of the order of a picosecond) makes the significance of quantum propensity rules in collisions of large *highly excited* polyatoms unlikely.

Lastly, another classical artifact has been noted by Bruehl and Schatz [5] who have devised an elegant method that simultaneously solves the energy transfer and master equation problems using classical trajectories. They note that with CS_2, a very small substrate molecule, there is an extremely slow relaxation (of the order of nanoseconds) which arises from slow internal energy redistribution between collisions. This problem should not occur in the method we follow here, which looks at the collision dynamics on the timescale of a fraction of a picosecond, with a *coarse-grained* master equation used to relate the data so obtained to the experimental observables. The coarse graining implicitly assumes scrambling of energy between collisions.

3. Experimental test of postulates

The argument about interference between high partial waves is of course non-rigorous and indeed cannot be properly quantified if we restrict ourselves to elastic scattering alone. How could the foregoing supposition be proved? The only convincing theoretical proof would be for a proper quantum inelastic scattering calculation. Unfortunately, as stated, a complete quantum calculation, using the equivalent of eq. (3), is currently impossible for systems sufficiently large, and at sufficiently high energy, to be of interest.

A simple experimental test of the hypothesis is as follows: if the effect is indeed quantum mechanical in nature, it will show a strong mass dependence. Thus, there should be a large change in the energy transfer rate if the bath gas were changed from ^{4}He to ^{3}He. We propose that such an experiment should be carried out.

Any observation that ^{3}He gave a significantly different experimental value for $R_{E',2}$ compared to ^{4}He would strongly suggest that the low energy transfer rate compared to that predicted classically arose from the "high partial wave interference" effect suggested above. This is because the interaction potential is the same for each collision partner, and any "intramolecular" quantum effect (such as that caused by zero-point energy noted above) would not be significantly affected by a change in the mass of the collision partner. On the other hand, the interference between higher partial waves would depend strongly on the mass of the collision partner.

Finally, we note that the possibility of zero-point energy effects causing the discrepancy (which we feel is unlikely) could be tested by seeing if there were a significant difference in the energy transfer rates of azulene and azulene-d_8.

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