Quasiresonant Energy Transfer in Ultracold Atom-Diatom Collisions

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Quantum and classical quasiresonant vibration-rotation energy transfer is investigated for ultracold He-H_2 collisions. Classical trajectory computations show that extremely strong correlations between Δj and Δv persist at low energies, though the changes themselves are less than one quantum. Quantum computations show that quasiresonant transitions occur in the limit of zero collision energy but that threshold effects become important and that some quasiresonant channels close. The qualitative similarity between classical and quantum results suggests that they share a common mechanism. [S0031-9007(99)08787-6]

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Collisions between atoms and rotationally excited diatoms can cause energy to be transferred between the diatom's internal vibrational and rotational degrees of freedom. When the collision time is longer than the rotational period, the vibration-rotation energy transfer can be unusually efficient and specific [1]. This effect has been named quasiresonant vibration-rotation energy transfer, which for brevity we will refer to as QR transfer.

The first experimental demonstration of QR specificity was the rule $\Delta j = -4\Delta v$ found in collisions between rotationally excited Li_2^* and noble gas atoms [1], where $\Delta j \equiv j_f - j_i$ is the change in the rotational quantum number of the diatom, and $\Delta v \equiv v_f - v_i$ is the change in its vibrational quantum number. This inelastic channel dominated all others over significant parameter ranges of the collision. Classical calculations indicated that the transition is caused by a series of "collisionettes" that occur when the rapidly rotating diatom is stretched to its outer turning point and collinear with the atom [2].

QR transfer has since been found in a wide variety of collision species and interaction potentials. The general rule followed by quantum QR collisions is that a single channel,

$$\Delta I = n_v \Delta v + n_j \Delta j = 0 , \tag{1}$$

dominates, where n_v and n_j are small integers. This is connected to the fact that the adiabaticity of the action $I \equiv n_v v + n_j j$ is a factor in the collisions [3]. The quasiresonant condition [2]

$$n_v/n_j \approx \omega_v/\omega_j \tag{2}$$

also holds, where ω_v and ω_j are the classical vibrational and rotational frequencies of the diatom. This implies that the vibrational and rotational motion are in approximate low-order resonance. Equations (1) and (2) yield

$$\Delta E_{\text{int}} = \frac{\partial H}{\partial v}\Delta v + \frac{\partial H}{\partial j}\Delta j = \hbar\omega_v \Delta v + \hbar\omega_j \Delta j \approx 0 , \tag{3}$$

which is the condition that the internal energy of the diatom isapproximately constant.

Classically it is found that Eq. (1) holds nearly exactly, at the expense of Eq. (2), even for individual trajectories, which is initially surprising since there is no *a priori* requirement for the ratios of classical action changes to be small rational fractions. Classically very often a single pair of integers (n_v, n_j) dominates all other processes by a wide margin for a range of initial collision velocities and initial v and j. At low collision energies, the magnitude of Δv or Δj is usually much less than a single quantum, making the classical analog of the quantum process strictly speaking forbidden. Yet, it is surprising that the classical action changes are pointing in the right direction, with $n_v \Delta v + n_j \Delta j \approx 0$. In many circumstances, the rule is satisfied astoundingly well—ΔI in Eq. (1) can be 4 or more orders of magnitude smaller than the typical changes in v or j.

The essence of the adiabatic action is that the collision is slow compared to the rate of change of the angle conjugate to I, so slowing down the collision further could be expected to make matters even better for QR transfer. However, new factors at ultralow energy make this a richer question than it first appears: First, quantum reflection (threshold behavior) sets in at sufficiently low energy [4], possibly changing the collision mechanism. The reflection phenomenon is a clear deviation from classical behavior, so it might be possible for classical and quantum QR collisions to differ qualitatively at low energy. The onset of the threshold law regime depends on properties of the interaction potential, whereas QR

transfer at higher energies seems to be insensitive to all but the grossest qualitative properties of the potential [1]. Second, in QR collisions a bit of translational energy is either taken from or supplied to the diatom in order to keep action I fixed. What happens when this energy is no longer available? Quantum mechanically, some of the most important QR channels can become closed. Finally, classical collisions can last a long time, opening the possibility of chaotic scattering. These factors make the study of the ultralow energy QR collisions quite interesting.

Experiments of quasiresonant transfer have been described in detail [5] for collisions of rotationally excited Li_2^* with noble gas atoms for relative collision velocities ranging from 500 to 3000 m/s. The final state specificity is enhanced when the collision velocity is decreased. Classical trajectory [1,2,5,6] and quantum mechanical calculations [7] of inelastic cross sections have also demonstrated that the quasiresonant correlation improves as the collision velocity is decreased.

It has been suggested that QR transfer may be an important relaxation mechanism for trapped H_2 molecules and may provide an inversion mechanism in rotationally pumped lasers [1]. The possibility of ultracold molecule formation [8] has motivated recent studies of collisional quenching [9] and opens a new window for investigation of QR transfer in the ultracold regime.

In the present work, we investigate quasiresonance in ultracold ^{4}He-H_2 collisions by computing trajectories for the classical system and by computing cross sections and rate coefficients for the quantum mechanical system. Although it is believed that QR transfer is insensitive to the details of the potential energy [1], we performed our classical and quantum calculations using a reliable surface—the H_2 potential of Schwenke [10] and the He-H_2 interaction potential of Muchnick and Russek [11]. We find that QR energy transfer persists at ultralow energies, but with modifications. Classically, the correlation implied by Eq. (1) remains strong despite the fact that many collisions result in the collision partners sticking together for several rotations; however, in most cases the collisions transfer only a tiny fraction of a quantum between j and v. Quantum mechanically, we find that energy conservation forbids what would otherwise be the strongest QR transitions. Meanwhile, sharp threshold behavior appears in the zero-temperature quenching rate coefficient when the final collision velocity approaches zero. But despite these new aspects, quasiresonant transfer is found to be an important effect in ultracold collisions, both classically and quantum mechanically.

Classical results.—Classical calculations are slow at low collision energies because the integration time step is dictated by the vibrational period, whereas the time of the collision scales like $E^{-1/2}$. We chose the collision energy $E_i = 10^{-6}$ a.u. $= 2.7 \times 10^{-5}$ eV $= 0.32$ K for the classical trajectories shown here, which is a factor of 40 smaller than the van der Waals attractive well between He and H_2. To simulate initial H_2 quantum numbers (v_i, j_i), we chose the diatom's initial radial action and internal angular momentum to satisfy the semiclassical quantization conditions $\oint p_r\, dr = 2\pi\hbar(v_i + 1/2)$ and $|\mathbf{J}_i| = \hbar(j_i + 1/2)$. For each (v_i, j_i), we computed 1000 classical collision trajectories with random initial conditions and impact parameters $|b| \leq 20$ a.u. Then we inverted the above relationships to find the final "quantum numbers" (v_f, j_f) of the diatom, which in general are not integers because the calculations were purely classical.

In ultracold collisions, it was not known whether classical QR transfer occurs at all. Indeed it does, for example, as seen in Fig. 1 for $(v_i, j_i) = (2, 21)$. For these initial conditions, $\omega_v/\omega_j \approx 2.079$, and accordingly the collisions all have action changes very close to the nearby rational line $\Delta j = -2\Delta v$. We thus see that the classical QR correlation persists at very low energies. On the other hand, at these low energies, Δv and Δj are much smaller than one quantum, so state-to-state transitions do not occur classically. Nevertheless, the strong classical correlation between Δj and Δv suggests that an analogous correlation is likely in the quantum reaction rates.

Higher-energy diatom-atom collisions have been described as a series of discrete collisionettes, one per half-rotation of the diatom, between which the interaction potential energy drops by several orders of magnitude [2]. Ultracold collisions are far gentler; instead of distinct collisionettes there is only a strong modulation of the interaction potential at frequency $2\omega_r$ (Fig. 1 inset). Thus the

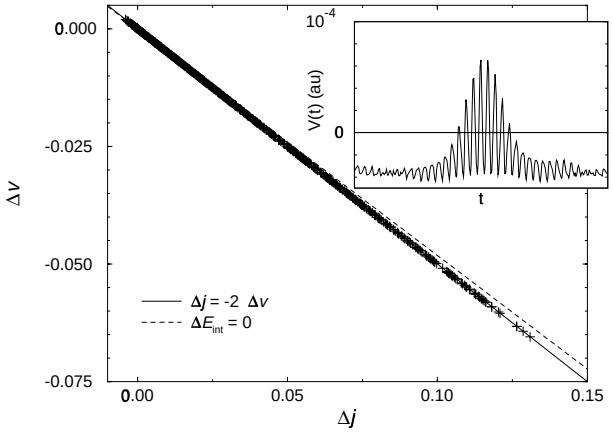

FIG. 1. A scatter plot of Δv versus Δj for 1000 classical collisions with $v_i = 2$ and $j_i = 21$. The quasiresonant prediction for this case is $\Delta j = -2\Delta v$, shown as a solid line; the maximum deviation from that line is 5×10^{-6}. The dashed curve is the energy limit, which crosses the QR line slightly above $(0, 0)$ [it would cross exactly at $(0, 0)$ if E_i were exactly zero], and is responsible for the fact that most collisions have $\Delta j \geq 0$ and $\Delta v \leq 0$. Inset: the He-H_2 interaction potential $V(t)$ during the repulsive part of a typical collision; the modulations are at frequency $2\omega_r$.

collisionette picture does not apply at ultralow energies, and the more general adiabatic treatment [3] is more appropriate.

What of long-time classical collisions? We find many collisions in which the colliding particles become loosely bound for several orbits and experience several successive subcollisions (each much like the one shown in the inset in Fig. 1). The number of subcollisions is a sensitive function of initial conditions. Nevertheless, each subcollision obeys the QR rule separately, and so therefore does the total collision.

Figure 2 shows the rms change in v and j observed in classical trajectory calculations for $v_i = 2$ and $1 \leq j_i \leq 28$. (For $j > 28$ the diatom is no longer bound.) In each of the peaks, Δv and Δj for the individual trajectories tend to become large and highly correlated, with the rational ratios n_v:n_j shown. The strongest quasiresonant transitions occur near $j_i = 9$, where $\omega_v/\omega_j \approx 4.03$ and n_v:$n_j = 4$:1, and near $j_i = 23$, where $\omega_v/\omega_j \approx 1.94$ and n_v:$n_j = 2$:1.

The peak at $j_i = 1$ corresponds to $\Delta j \neq 0$, $\Delta v \approx 0$. Using our nomenclature, it has a ratio n_v:$n_j = 1$:0, though of course it is not a quasiresonant transfer but rather a pure rotational transition. It, plus the other two shaded peaks, will be seen to have analogs in the quantum system.

Quantum results and threshold behavior.—The quantum mechanical formulation and the methods used to obtain the cross sections have been described previously [9]. As a consequence of Wigner's threshold law, the quenching rate coefficients are independent of temperature below 10^{-3} K. Figure 3 shows ultracold quenching rate coefficients for $^4\mathrm{He} + \mathrm{H}_2(v_i, j_i)$ calculated quantum mechanically.

The results for $v_i = 2$ are shown as a function of j_i; data for other initial vibrational quantum numbers are similar and will be presented elsewhere. The three most important transitions are seen to be pure-rotational transitions plus the two quasiresonant transitions $\Delta j = -4\Delta v$ and $\Delta j = -2\Delta v$. Each is centered at approximately the same initial j value as the analogous classical peak. But, there are differences: (a) Where the classical QR peaks are strongest, the quantum peaks have gaps; (b) the rules corresponding to the small classical peaks (8:1, 6:1, 3:1, and 8:3) are absent in the quantum data; (c) the quantum transition rates show decreases near the gaps; and (d) the heights and widths of the quantum peaks are not clearly related to those of the classical peaks. Investigating those differences will lead us to a better understanding of quantum QR transfer.

For zero-temperature collisions, there is no kinetic energy available to increase the energy of the diatom, so only transitions with $\Delta E_{\mathrm{int}} \leq 0$ are energetically allowed. Classically, it is always possible to find small Δv and Δj that satisfy both the QR and the energy conditions. Therefore, classical QR transfer is energetically possible for any initial state. Quantum mechanically, however, v and j must always change by an integer, and it sometimes happens that all final quantum states satisfying the QR condition have a higher energy than the initial state. Thus, for some initial states, there are no open quasiresonant transition channels. For example, the classical collisions for $(v_i, j_i) = (2, 22)$ obey a very strong 2:1 QR rule. However, the maximum action change that both satisfies the QR condition and is energetically allowed is $(\Delta v, \Delta j) \approx (-0.1239, 0.2478)$, which is less than one

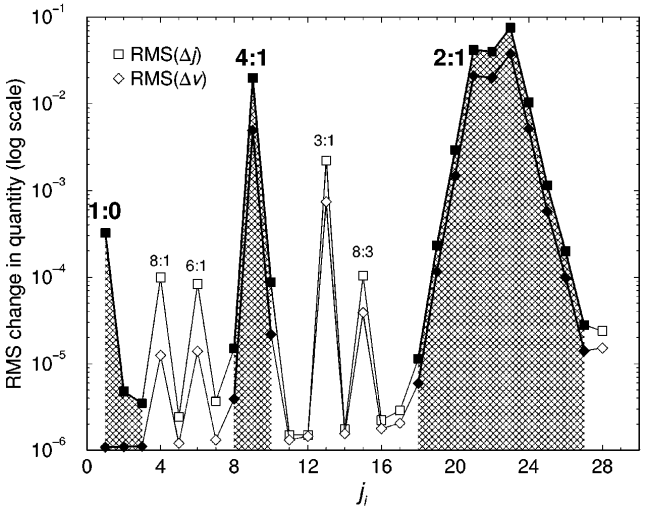

FIG. 2. Classical trajectory calculations of the root-mean-square (rms) changes to j and v as a function of j_i. Each peak corresponds to a quasiresonant transition satisfying Eq. (1), with the indicated ratio n_v:n_j. The shaded peaks are those that have analogs in the quantum rate coefficients (Fig. 3). The rms of the deviation ΔI [Eq. (1)] is less than 10^{-5} for all QR cases.

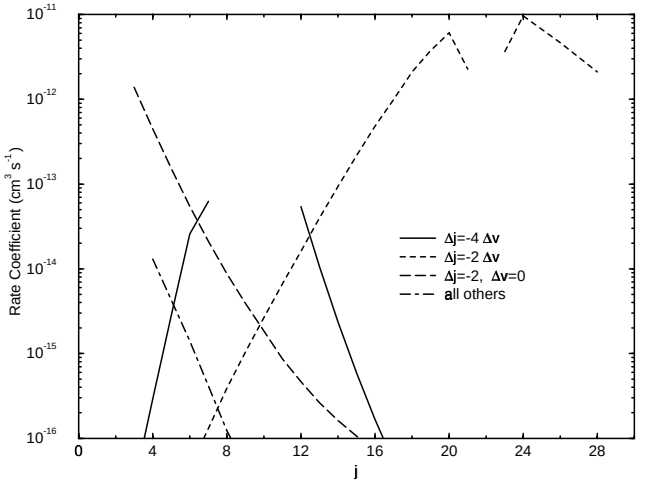

FIG. 3. Quantum mechanical calculations of the zero-temperature quenching rate coefficients as a function of j_i for $v_i = 2$. Solid curve, $\Delta j = -4\Delta v$; dotted curve, $\Delta j = -2\Delta v$; dashed curve, all other transitions.

quantum. Therefore the 2:1 QR channel is not available from the initial state $(2, 22)$, and Fig. 3 shows a gap. Similarly, the 4:1 QR channel shows a gap for $7 < j_i < 12$. Generally the left hand side of a gap corresponds to $\Delta j > 0$ and the right hand side to $\Delta j < 0$.

Energy conservation also prevents the smaller classical QR peaks (8:1, 6:1, 3:1, and 8:3) from appearing at all in the quantum data—there are no open channels from the corresponding initial states with those ratios of changes in quantum numbers.

When quantum transitions are close to the energetic limit, they are subject to threshold behavior. In Fig. 3, threshold structure appears as a noticeable suppression of transition rates for $(2, 7) \rightarrow (1, 11)$, $(2, 21) \rightarrow (1, 23)$, and $(2, 23) \rightarrow (3, 21)$ transitions. The sudden decrease in the zero-temperature quenching rate coefficient at values of j near thresholds can be understood from the asymptotic form of the inelastic cross section,

$$\sigma_{if} \sim k_i^{2l_i-1} k_f^{2l_f+1}. \quad (4)$$

At ultracold temperatures, $l_i = 0$ and the rate coefficient, which is equal to the collision velocity times the cross section, vanishes as $k_f^{2l_f+1}$, where $l_f = |\Delta j|$.

In conclusion, quasiresonant energy transfer is said to occur when an inelastic transition is highly specific and efficient [1]. For values of j_i for which $\Delta j = 4$ is energetically possible, $\Delta v = -1$, $\Delta j = 4$ transitions dominate all other $\Delta v = -1$ transitions in the low temperature limit. These transitions, however, are not strictly quasiresonant since the pure rotational quenching rates for these values of j_i are even larger (see Fig. 3). The $\Delta v = -1$, $\Delta j = 2$ transition rates, on the other hand, are substantially larger than all other inelastic rates for $12 < j_i \leq 21$, including the pure rotational quenching rates. These quasiresonant transitions are very efficient and may be a good candidate to provide a rotational inversion mechanism [1] at ultracold temperatures. Similarly, the $\Delta v = 1, \Delta j = -2$ transitions, for $23 \leq j_i \leq 28$, are quasiresonant by the strict definition.

In this work, we performed a detailed investigation of quasiresonant energy transfer in He-H_2 scattering and found that it persists to ultracold temperatures both in classical mechanics and in quantum mechanics. If the quasiresonant process for ultracold collisions is insensitive (as it is for higher temperature collisions) to the nature of the interaction potential, then the rovibrational dependence of the zero-temperature quenching rates for other atom-diatom systems should be qualitatively similar to the results presented here. However, it is quite possible that the low-temperature behavior is significantly different for interactions that have no attractive part.

We have shown that there are rough analogies between the classical and the quantum QR behavior. However, whether the quantum reaction rates could be quantitatively derived from classical trajectories at these low temperatures is not yet clear. Doing so would appear to require a treatment similar to that of resonant dynamical tunneling processes [12], with the added complication of quantum suppression of the near-threshold semiclassical trajectories [4].

We have found that the classical phenomenon of quasiresonant energy transfer is a general feature of low energy collisions, and some of its aspects should be found in systems with more internal degrees of freedom. Diatom-diatom collisions, for example, would allow an interesting extension of the quasiresonance phenomenon presented here. The essential ingredient is nearly conserved actions, which are the result of an adiabatic collision with respect to "fast" combinations of the original actions. We hope that the realization of trapped molecules will provide an opportunity for experimental investigations of ultracold quasiresonant energy transfer.

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