Dynamics of Quasiresonant Vibration-Rotation Transfer in Atom-Diatom Scattering

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Quasiresonant vibration-rotation transfer in the collision of an atom with a diatomic molecule is studies with use of classical trajectories. At high molecular rotation rates and low collision velocities the atom-diatom interaction consists of a sequence of small collisions ("collisionettes"). This leads to a nearly perfect negative correlation between the changes in the rotational and vibrational actions and very large vibrationally inelastic cross sections. This quasiresonant process shows evidence of frequency locking between the vibrator and the rotational "oscillator."

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We present a study of the dynamics of a recently discovered process in atom-diatom collisions which has been experimentally observed,[1-4] and has been seen previously in calculations.[5-10] Quasiresonant vibration-rotation (V-R) transfer, a special case of the three-body problem, occurs in atom-diatom collisions at high initial molecular rotation levels[1,2] and low collision velocity.[4] Its qualitative features are remarkably independent of both initial vibrational level[2] (v_i) and collision partner[3] (interaction potential). It is characterized by large vibrationally inelastic cross sections with very narrow final rotational state (j_f) distributions. The peak position of each j_f distribution is correlated with $\Delta v \equiv v_f - v_i$; in $\mathrm{Li}_2{}^*$-rare-gas measurements[2,3] the peak $\Delta j \equiv j_f - j_i$ shifts according to the rule $\Delta j^{\text{peak}} = -4\Delta v$. Our classical-trajectories study not only reproduces these features (see Ref. 2) but, more importantly, elucidates the novel dynamics involved in quasiresonant V-R transfer and suggests a link between this process and the phenomenon of frequency locking familiar in nonlinear dynamics.

Our classical-trajectories program is formulated with action-angle variables[11] and represents the first application of these variables to a dynamically exact 3D problem with coupled orbital, rotational, and vibrational actions. Action-angle variables not only speed the calculation[12] but also allow us to follow the time evolution of the observable quantities (v and j) throughout the collision. We can expect classical mechanics to be valid in the regime studied here.[13]

To demonstrate the onset of quasiresonant V-R transfer, Fig. 1 displays the results of calculations for $\mathrm{Li}_2{}^*$-Ne collisions. In each of the graphs, v_i, J_i, and the initial relative velocity v_{rel} were held constant while all other parameters (i.e., impact parameter, orientation, and initial phases of rotation and vibration) were chosen at random. One dot is plotted for the final outcome[14] (Δv,Δj) of each trajectory; the cross section is proportional to the density of dots. The cross section is large close to the intial level as a result of nearly elastic trajectories. Since each of Figs. 1(a)-(c) presents the same number of trajectories (20000), the large dot density along the line in Fig. 1(c) implies very large cross sections to final levels near this line (e.g., ≈ 16 Å^2 into the single final level $\Delta v = -1$, $\Delta j = +4$).

Figure 1 reveals the development of a striking correlation between Δv and Δj as j_i increases and v_{rel} decreases, just as is observed in measurements.[2,4] This correlation is manifest in experiments as very narrow j_f distributions at each v_f, and as a linear shift of Δj^{peak} with Δv. In Fig. 1(a), there is only moderate correlation between Δv and Δj. However, in Fig. 1(b) at higher j_i, Δv and Δj are highly correlated, and in Fig. 1(c), at decreased v_{rel}, the linear correlation is virtually perfect. These calculations were repeated for a wide range of j_i; the slopes $\Delta j/\Delta v$ [shown in Fig. 2(a)] cluster around the even integer nearest to $-\omega_V/\omega_R$, where ω_V is the vibrational frequency and ω_R is the initial rotational frequency. The reason the slope is "quantized" in this way, and why the $\Delta j/\Delta v$ correlations [like Fig. 1(c)] are so straight, is, as yet, unclear. This collisional process was termed quasiresonant because this "quantization" causes the slopes to deviate from the energy-resonant line in Fig. 2(a).

In general, our calculations[15] and experiments[2] contain highly correlated outcomes [i.e., like those in Fig. 1(c) or Fig. 2] whenever the rotational frequency is a significant fraction of the vibrational frequency and the collision duration is longer than the rotational period. In this very nonsudden regime the temporal behavior of the interaction force is largely determined by the internal motions of the molecule (the rotation and vibration). As Blais and Truhlar[16] pointed out, the driving force on the vibrational oscillator contains much higher-frequency components due to the rotational motion than it would from the translational motion alone, enhancing the probability of change in the vibration. However, high-frequency components of the force do not alone lead to vibrational transfer. For example, in the different regime of *low* j_i and low velocity, rapid modulations of the force result entirely from the vibrational motion, resulting in *large* force pulses at the vibrational frequency.

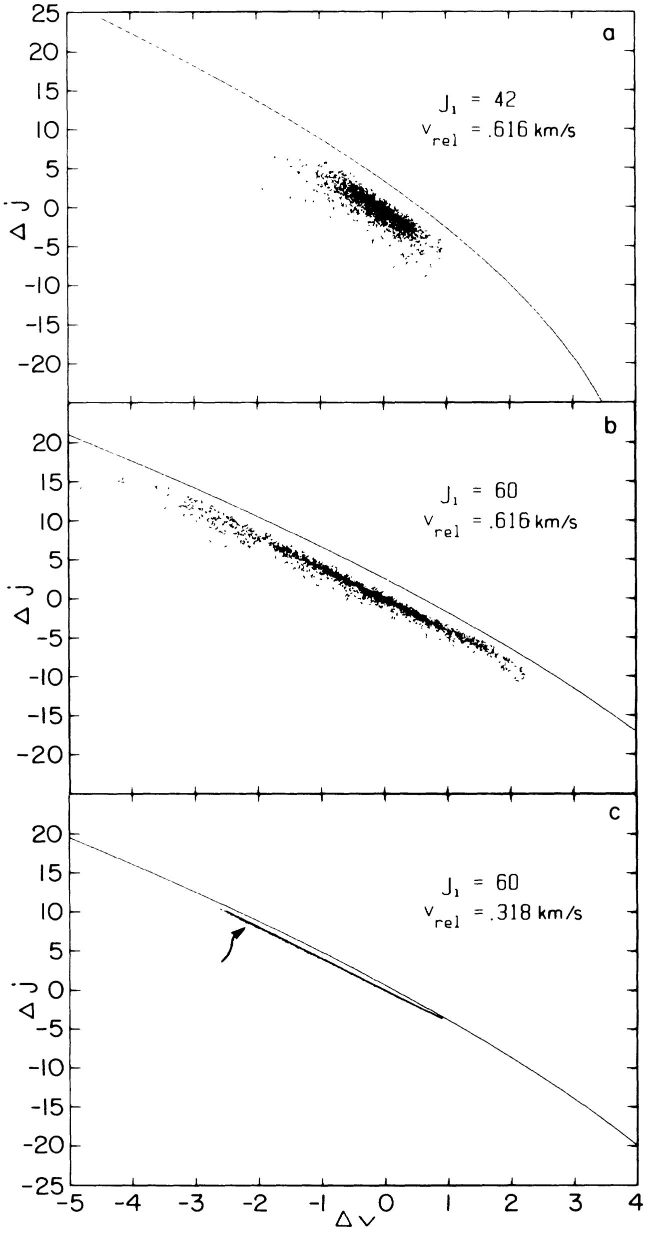

FIG. 1. Collisional outcomes Δj vs Δv from Li_2^*-Ne collisions with $v_i=9$ and (a) $j_k=42$, $v_{rel}=0.616$ km/s; (b) $j_i=60$, $v_{rel}=0.616$ km/s; (c) $j_i=60$, $v_{rel}=0.318$ km/s. All other initial conditions were chosen at random. The relative kinetic energies and correlation coefficients are (a) 131 cm^{-1}, −0.6057; (b) 131 cm^{-1}, −0.9757; and (c) 35 cm^{-1}, −0.9999. The solid curve is the energy limit. Note in (b) and (c) that the dots fall on a straight line although the energy limit is curved.

However, the temporal symmetry of these pulses about the vibrational outer turning point suppresses the vibrational transfer. Rapid rotation, on the other hand, not only supplies force components at the vibrational frequency, but shifts the timing of the driving impulses away from the outer turning point, causing substantial vibrational excitation.

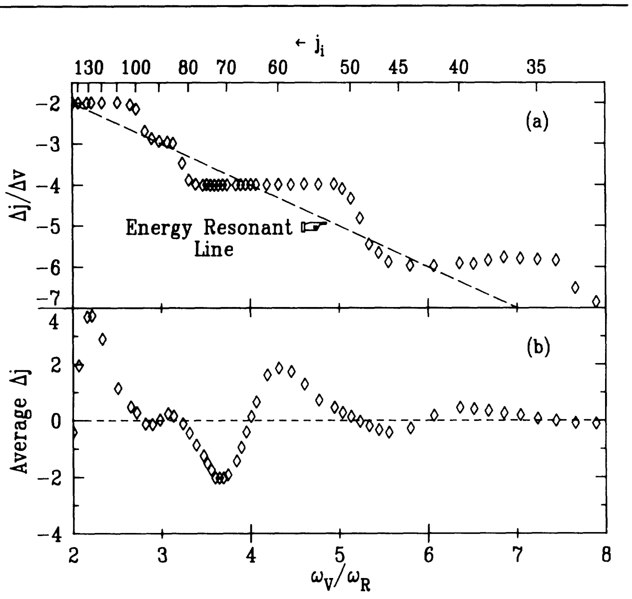

FIG. 2. Variation of (a) $\Delta j/\Delta v$ and (b) the average Δj with the ratio of the vibrational to initial rotational frequencies ω_V/ω_R. Each point is calculated from results like those shown in Fig. 1 (at the j_i shown along the top) where the slope of the resulting line of dots is $\Delta j/\Delta v$. Each point is the result of 1000 to 5000 trajectories with $v_{rel}=0.318$ km/s and $v_i=9$. The dashed line in (a) is of slopes which would conserve internal energy. Note that integer values of ω_V/ω_R (except 5 and 7) result in transfer with an energy-resonant $\Delta j/\Delta v=\omega_V/\omega_R$ there, and $\Delta j_{avg}=0$.

The dynamical origin of this shift of the impulses away from the vibrational turning point, which also gives rise to the Δv-Δj correlation, can be seen in Fig. 3. This figure displays, for a single collision, the temporal development of v, j, the internuclear separation of the molecule ($r\equiv|\mathbf{r}|$), and $\cos^2\gamma$, where $\mathbf{r}\cdot\mathbf{R}=rR\cos\gamma$ and $\mathbf{R}$ is the vector from the center of mass of the diatom to the atom. The interaction potential $V=V(R,r,\cos\gamma)$ between the molecule and the atom, shown at the bottom of Fig. 3, is modeled as an exponentially repulsive breathing ellipsoid.[17]

This collision, like the majority shown in Fig. 1(c), is composed of a sequence of subcollisions that we term "collisionettes." Each collisionette resembles a separate collision; between collisionettes the interaction potential energy drops by several orders of magnitude and both the vibrational and the rotational actions settle to definite values. Collisionettes occur (i.e., the interaction energy peaks) whenever an end of the diatom passes near the atom. Specifically, collisionettes occur *between* the time when the molecular axis is nearest to collinear with the atom ($\gamma\cong 0$ or π) and the time when the vibration is at its outer turning point. For the relative phase of rotation and vibration shown in Fig. 3, the collisionettes occur just *after* the closest rotational approach to col-

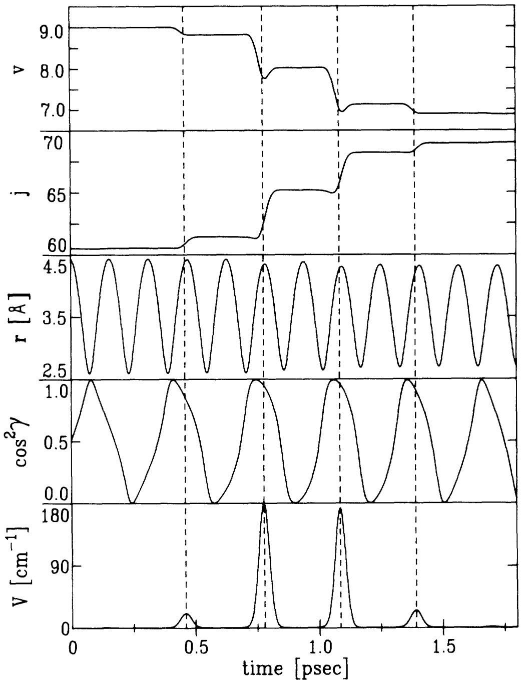

FIG. 3. Temporal development of selected dynamical variables during a single collision. They are (from top to bottom): the vibrational action v, rotational action j, internuclear separation r, $\cos^2\gamma$, (where γ is the angle between the axis of the diatom and a line from the diatom to the atom), and the interaction potential $V=V(R,r,\cos\gamma)$. Note that this collision is composed of four brief interactions (termed "collisionettes") centered on the dashed lines, and that each changes v and j in a correlated fashion. The final outcome of this collision is indicated by an arrow in Fig. 1(c) and its trajectory is nearly in the plane of the molecular rotation with impact parameter $b=0.82$ Å (compared with $2.6\text{ Å}\leq r\leq 4.4$ Å, at $v=9$, $j=60$).

linear orientation and just *prior* to the vibrational outer turning point. Thus, the effect of the (repulsive) force in each collisionette is to reduce the vibrational action and boost the rotational action of the diatom, producing the observed negative correlation of Δv and Δj. If the initial phase difference between the rotation and the vibration in any collisionette were reversed, the signs of both Δv and Δj for that collisionette would also be reversed, preserving the negative correlation. Since collisionettes occur near the ends of the fully extended molecule, they can occur for large impact parameters, yielding large cross sections.

For the conditions of Fig. 1(c), all collisions that are significantly inelastic are composed of collisionettes, including collisions at almost all orientations and impact parameters. Collisions without collisionettes do occur for severly out-of-plane trajectories at small impact parameters but are elastic and do not contribute to the V-R transfer.

Whenever ω_V/ω_R is an even integer,[18] an integral number of complete vibrations takes place during each half rotation, and successive collisionettes occur with the same phase relationship between $\cos^2\gamma$ and r. In this case, successive collisionettes act additively to produce a larger overall change in v and j for that collision. When j is not exactly at such a "resonance," all collisionettes within a collision need not have the same sign of Δj, and successive collisionettes may act subtractively resulting in a smaller total Δv and Δj for the whole collision. If the first few collisionettes change j toward the nearest resonance, subsequent collisionettes will then act coherently and a larger Δj will result than if the initial collisionettes had changed j away from the resonance.

Because changes of j toward a resonance result in larger Δj than changes in the opposite direction, averaging over may collisions yields Δj_{avg} such that the average final j is nearer the resonant value [Fig. 2(b)]. In effect, the interaction with the target atom acts as a nonlinear coupling between the vibrational and rotational oscillators, causing ω_R to be pulled toward an even integral submultiple of ω_V (i.e., where ω_V/ω_R is an even integer). This phenomenon is known as frequency locking or entrainment[19] in the case of a continuous, rather than transient, coupling.

Quasiresonant V-R transfer has been observed with many different interaction potentials and at various v_i. All of the trajectories plotted in this paper were calculated with an exponentially repulsive breathing ellipsoid potential,[17] but plots of Δj vs Δv similar to Fig. 1 were also made with other potentials. We have tested potentials which were the sum of two two-body repulsive terms, with both terms varying either exponentially, as an inverse power, or linearly with the distance. Quasiresonant V-R transfer was observed for each of these and also for a potential with a long-range attractive tail (well depth $=1.43E_{\text{rel}}$). The single exception found was for an unrealistically hard potential[20] that forced the collisions to be impulsive. Quasiresonant transfer has also been seen with other potentials in calculations of H_2-H,[7] H_2-He,[5,6] H_2-Ar,[10] HCl-Ar,[8] and OH-Ar (Ref. 9) collisions, although its origins have remained obscure until this work. Experimental evidence also suggests qualitative insensitivity to the potential and v_i, since quasiresonant transfer has been observed in Li_2^*-X systems[3] with X = Ne, Ar, and Xe, among which the interaction potentials are very different, and with Ne and Xe for v_i from 4 to 9.[1-3] We have also conducted calculations with v_i ranging from 0 to 9 and always find quasiresonant behavior (although the size of the cross sections increases somewhat with v_i, in part because of the larger average "size" of the molecule). Details will be presented in a future work.[15]

We have elucidated much of the origin of quasiresonant V-R transfer. Diatomic collisions at high j and low velocity are composed of collisionettes. These lead to a negative correlation between Δv and Δj for nearly all initial orientations and impact parameters. The result is large cross sections with highly specific final-state distributions. Challenges remain though: to explain why the correlation curves of Δj vs Δv [e.g., Fig. 1(c)] are so perfectly straight, and why their slopes persist at constant values over wide ranges of j_i [Fig. 2(a)]. Also, why are the preferred slopes precisely equal to integer ratios of the vibrational and rotational frequencies? If, as we suggest, these results are a manifestation of a frequency-locking mechanism, it would be of fundamental interest to study it within a fully quantal calculation. Such a calculation is also mandated in order to remove uncertainties caused by the quasiclassical binning[2] of final-state distributions that have features on a scale smaller than the bin widths, as they do in these results.

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[12] The vibrational action v and its phase velocity vary much more slowly (and not at all in the absence of the atom-molecule interaction) than the internuclear separation r and its conjugate momentum p_r. Thus the minimum integration time step required to follow pertinent changes with action-angle variables is much longer than if r and p_r were used as the variables.

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[14] In this paper, v_f and j_f (and so Δv and Δj) take on continuous values to present best the results which follow. This is unlike the more common quasiclassical trajectories, where v_f and j_f are constrained to integer values.

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[17] The analytic form is very similar to previously proposed models [N. Smith, Ph.D. thesis, Massachusetts Institute of Technology, 1983 (unpublished), and Ref. 11]:

$$V(R,r,\cos\gamma)=V_1\exp\left\{\frac{-R+\alpha(r-r_0)[1+aP_2(\cos\gamma)]}{L\{1+[1-\beta(1-r/r_0)]aP_2(\cos\gamma)\}}\right\},$$

where $V_1=759$ eV, $L=0.381$ Å, $a=0.325$, $\alpha=0.566$, and $\beta=0.5$.

[18] For a homonuclear diatom, the rotation causes identical impulses at a rate of $2\omega_R$; hence the resonant frequency ratios must be even.

[19] R. H. Abraham and C. D. Shaw, *Dynamics: The Geometry of Behavior, Part One: Periodic Behavior* (Aerial, Santa Cruz, CA 1982), p. 175.

[20] The potential in footnote 17 was made very hard by use of $L=0.04$ Å. This is a much smaller scale length than any actual molecular potential.