Zero-Energy Resonances of Hydrogen Diatom Isotopologs: Tuning Quasiresonant Transitions in Vibration Space

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(Received 7 August 2012; published 4 December 2012)

Highly efficient and specific energy transfer mechanisms that involve rotation-rotation, vibration-vibration, and vibration-rotation exchange in diatomic molecules are examined theoretically in ultracold H_2, D_2, and HD self-collisions as a function of initial vibrational level v. The three quasiresonant mechanisms are found to operate for all vibrational levels and yield complex scattering lengths which vary smoothly with v. Exceptions to this trend occur at select high values of v where the scattering lengths are modulated by orders of magnitude corresponding to the location of an s-wave zero-energy resonance in "vibration space." The quasiresonant mechanisms, which are not very sensitive to the details of the interaction potential, generally control the final distribution of molecular states for any given initial distribution. The zero-energy resonances are more sensitive to the potential and may be used to vibrationally "tune" the interaction strength, similar to methods which vary applied external fields.

DOI: 10.1103/PhysRevLett.109.233201 PACS numbers: 34.50.Cx, 34.50.Ez

Experimental and theoretical investigations of molecular scattering at ultracold temperatures are a rapidly growing area in atomic and molecular physics and chemical physics [1–7]. When two molecules collide at ultralow temperatures, their dynamics is controlled by threshold phenomena and resonances providing sensitive probes of interactions which govern chemical processes. In some cases, the internal energy transfer can be unusually efficient and specific. Such cases are often referred to as "quasiresonant" [8]. For example, quasiresonant vibration-rotation (QRVR) energy transfer occurs in atom-diatom collisions when the ratio of the rotational and vibrational periods of the diatom is nearly equal to an integer. Such propensity rules have been observed experimentally at ordinary temperatures [9,10]. The remarkable properties of QRVR energy transfer have stimulated a number of theoretical studies [10–15] which have shown that the classical dynamics of the system generally plays a significant role in the collisions. Calculations have also shown that the classical mechanism persists at ultracold temperatures [13]. The presence of a QRVR condition together with an ultralow collision energy can yield sharp structures in rotational distributions of total quenching rate coefficients [16–18] and may allow convenient detection for systems containing rotationally hot molecules [17–19]. While experimental schemes to form highly rotationally excited molecules have been proposed [20,21] and realized [22,23], most experimental approaches which produce translationally cold molecules, however, do not contain a significant population of rotationally excited states, so the interesting case of ultracold QRVR energy transfer has yet to be observed experimentally. Nevertheless, a very recent experimental study has demonstrated rotational excitation of translationally cold N_2 molecules [24]. A remarkable aspect of this study is the selective rotational excitation of both para- and ortho-N_2 as well as isotopologs of N_2 through quantum resonances. Experiments with ultracold H_2 molecules may also be possible using optical Stark deceleration and sympathetic cooling [25,26].

Anticipating that future experiments will be able to produce and study highly vibrationally excited, but translationally cold molecules, we have performed the first full-dimensional quantum calculations for vibrational levels up to the diatom dissociation limit for the H_2+H_2 collision system. In particular, we have identified an efficient QRVR mechanism that occurs for H_2 molecules with zero angular momentum, which is therefore considerably more amenable to experimental verification. We provide further elucidation of the quasiresonant rotation-rotation (QRRR) and quasiresonant vibration-vibration (QRVV) mechanisms that have been recently identified for the low vibrational levels of H_2 self-collisions [27–29]. We find that the efficiency and specificity of all three mechanisms extend the quantum scattering code to higher vibrational levels, but for certain select vibrational quantum numbers v the mechanisms are enhanced via the presence of a zero-energy resonance. Here, we attribute a zero-energy resonance to an s-wave bound or virtual state with energy sufficiently close to the complex's dissociation limit that structure emerges in the scattering length as a control parameter is varied. A zero-energy resonance can be identified by an abrupt change in magnitude and sign of the real part of the scattering length as a function of the control parameter. This phenomenon is observed for H_2, D_2, and HD self-collisions, though for HD the QRRR mechanism is suppressed at low v due to efficient $\Delta j = -1$ quenching, where j is the rotational quantum number.

In cold and ultracold collisions it is well known that the strength of elastic and inelastic processes can be modulated through the tuning of various control parameters. For example, an applied external field can be adjusted to tune the system to a Feshbach resonance [30]. Similarly, the collision system reduced mass (or interaction potential well depth) can be theoretically varied to locate zero-energy resonances or to modulate orbiting resonances [31]. We find here, that by varying v, the zero-energy resonance may be tuned to increase or decrease the interaction strength similar to methods which use external fields. This controls the efficiency of the energy transfer mechanisms and allows for even greater specificity in the distribution of molecular states. The quasiresonant mechanisms are what allow the vibrational quantum number to serve as this new control parameter.

In all three quasiresonant mechanisms, which are not present in collisions of molecules with atoms, the collision partners swap internal excitation resulting in large cross sections and scattering lengths. The efficiency of the QRRR and QRVV mechanisms is characterized by conservation of total system internal rotational angular momentum and by near conservation of internal energy. The QRVR mechanism introduces a small change in internal angular momentum in order to further reduce the change in internal energy. This additional flexibility in diatom-diatom collisions is a consequence of the vibrational degree of freedom of both collision partners. The change in internal angular momentum may occur in such a way that when one or both molecules undergo a rotational transition, the internal energy gap remains small. This type of QRVR process does not occur in atom-diatom collisions for low rotational levels due to the large energy gap associated with vibrational change.

Theoretical investigation of the three quasiresonant mechanisms considered in the present work requires a full-dimensional potential energy surface (PES) and a quantum mechanical description of all internal degrees of freedom. There is an extensive literature on $H_2 + H_2$ collisions using different PESs and quantum mechanical scattering formulations, so we do not provide a full discussion here (see Ref. [29] for details and references). The present calculations were performed using a modified version of the quantum scattering code TwoBC [32] with the modified Boothroyd-Martin-Keogh-Peterson PES [33]. The combined molecular state is used to describe each molecule before or after a collision with the vibrational and rotational quantum numbers v and j, respectively. The combined molecular state is denoted as $(v, j; v', j')$ with the "well-ordered" classification that $v > v'$ or when $v = v'$, $j \geq j'$ with the appropriate symmetrization for indistinguishable molecules. A truncated basis set tailored for each $(v, j; v', j')$ combination was adopted within the full close-coupling formalism.

Cross section calculations were performed at a collision energy of 10^{-6} cm^{-1}, which was found to be sufficient for describing the collision in terms of the complex s-wave scattering length $a = \alpha - i\beta$, where α and β are the real and imaginary components [34]. The magnitude and sign of the real part α depend on the position of the last bound or virtual state of the collision complex relative to the dissociation limit. The imaginary part β is related to the total inelastic quenching rate coefficient in the limit of zero velocity. The real part α can be determined from the

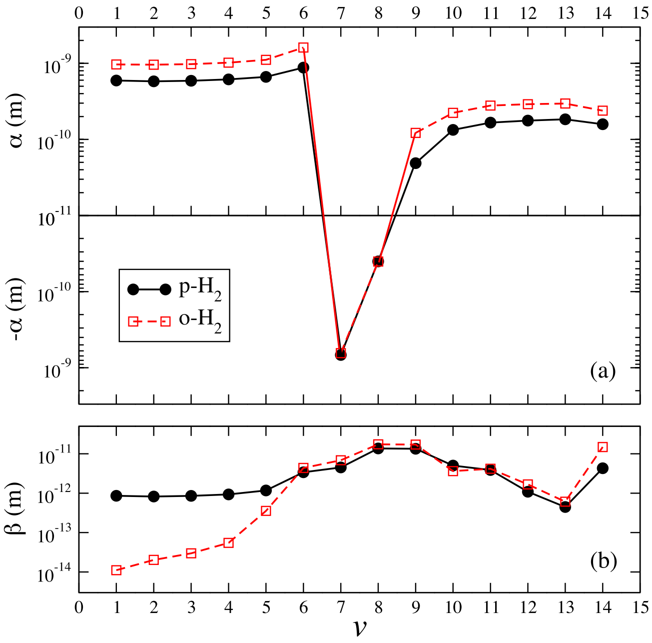

FIG. 1 (color online). Real component α (top panel) and imaginary component β (bottom panel) of the complex scattering length for $H_2 + H_2$ collisions for initial state $(v, j; v, j)$. Filled circle: para-H_2, $j = 0$; open square: ortho-H_2, $j = 1$. The value of β is dominated by QRVV transitions to $(v + 1, j; v - 1, j)$ for all v.

limiting s-wave phase shift, while its magnitude can be conveniently obtained from the elastic cross section.

Figures 1–3 show the real and imaginary components of the complex scattering length for $H_2 + H_2$ collisions. The initial state determines which mechanism operates. In all cases, the value of β is dominated by a single quasiresonant transition. For states with no internal rotational excitation such as the para-para $(v, 0; v, 0)$ and ortho-ortho $(v, 1; v, 1)$ states shown in Fig. 1, it is QRVV transitions to $(v + 1, 0; v - 1, 0)$ and $(v + 1, 1; v - 1, 1)$ that dominate the total inelastic cross sections in each case. For low v, the QRVV mechanism controls the quenching process with the efficiency being relatively constant with v. A dramatic increase in the efficiency occurs due to the presence of a zero-energy resonance in vibration-space between $v = 6$ and $v = 7$.

A similar pattern is seen for initial states which have internal angular momentum excitation, such as the para-para $(v, 0; v - 1, 2)$ and ortho-ortho $(v, 1; v - 1, 3)$ states in Fig. 2. For these states however, the QRRR mechanism controls the energy exchange, with in nearly all cases, the final states being $(v, 2; v - 1, 0)$ and $(v, 3; v - 1, 1)$, respectively. The zero-energy resonance, which is now located between $v = 7$ and $v = 8$ in vibration space, greatly enhances the QRRR energy transfer for both ortho-ortho and para-para collisions. Essentially the same behavior was found for initial $(v, j; v - 2, j + 2)$ and $(v, j; v - 3, j + 2)$ states.

For initial states which have zero internal angular momentum, but have v's that differ by at least one unit of vibration, there is the possibility of QRVR transitions. This may be seen in Fig. 3 for initial $(v, 0; v - 1, 0)$ states. QRVV transitions do not occur for these states when $v < 9$ due to a large internal energy gap. Instead, the QRVR mechanism dominates and transfers most of the internal energy to final $(v + 1, 0; v - 2, 2)$ states. Unlike the case of atom-diatom collisions, there is no requirement that the molecule be rotationally excited for this QRVR process to occur. The molecule which initially has lower vibration is found to obey a $\Delta j = -2\Delta v$ propensity rule analogous to that of atom-diatom collisions [9,10]. The other molecule experiences an increase in its vibrational level in order to maintain a small internal energy gap for the transition. As in the QRVV and QRRR processes discussed above, a zero-energy resonance occurs between $v = 7$ and $v = 8$ in vibration space which significantly enhances the efficiency of the QRVR mechanism. For initial $(v, 0; v - 1, 0)$ states with $v \geq 9$ and for initial $(v, 1; v - 1, 1)$ states, there is competition between the different mechanisms and the energy transfer is less specific.

For continuous control parameters (e.g., an external field) it is possible to tune the system exactly to the zero-energy resonance. For a discrete control parameter such as the vibrational quantum number, the best that can be done is to tune to the vibrational level that is closest to the zero-energy resonance. The existence of the zero-energy resonance may be verified by theoretically varying the reduced mass. We illustrate this for the para-H_2 case considered in Fig. 2. In Fig. 4, a resonance is found for $v = 7$ in both the quenching and elastic cross sections for an H atom mass of

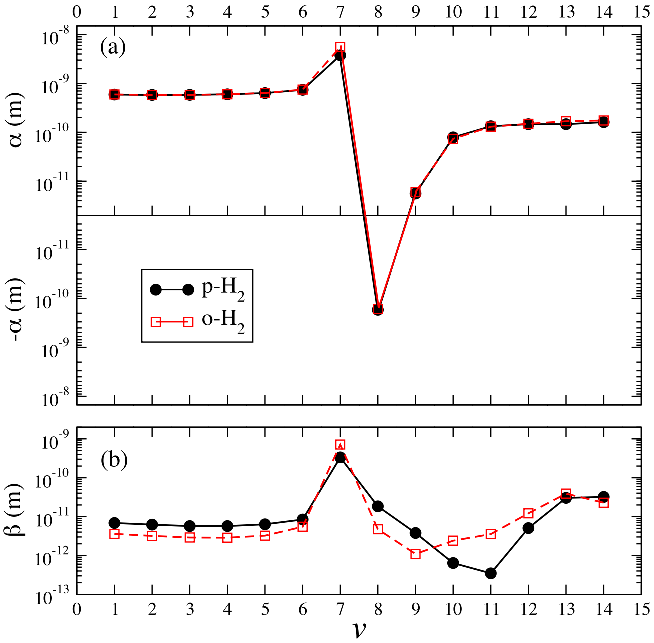

FIG. 2 (color online). Same as Fig. 1, except for initial state $(v, j; v - 1, j + 2)$. Filled circle: para-H_2, $j = 0$; open square: ortho-H_2, $j = 1$. The value of β is dominated by QRRR transitions to $(v, j + 2; v - 1, j)$ for all v.

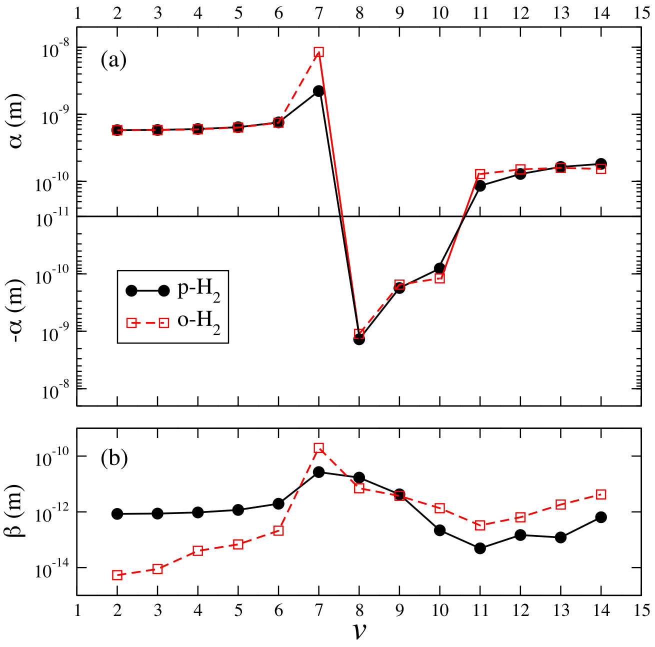

FIG. 3 (color online). Same as Fig. 1, except for initial state $(v, j; v - 1, j)$. Filled circle: para-H_2, $j = 0$; open square: ortho-H_2, $j = 1$. For para-H_2, the value of β is dominated by QRVR transitions to $(v + 1, j; v - 2, j + 2)$ for $v < 9$. For larger v and for ortho-H_2 collisions, the energy transfer is less specific due to competition between the different mechanisms.

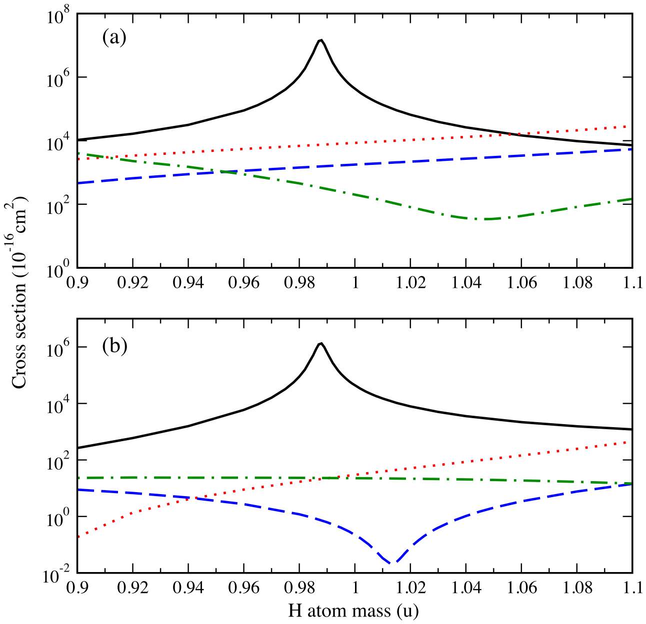

FIG. 4 (color online). Variation of (a) dominant state-to-state quenching and (b) elastic cross sections for $H_2 + H_2$ collisions for select initial states (v, 0; $v - 1$, 2) with H atom mass. Solid line: $v = 7$; dotted line: $v = 8$; dashed line: $v = 9$; dot-dashed line: $v = 11$.

0.988 u, being very near the physical H atom mass. For other values of v, the cross sections are seen to vary smoothly indicating that an s-wave bound or virtual state does not lie near a channel threshold. However, the elastic cross section may be "tuned" close to zero for $v = 9$ [compare to Fig. 2(a)] due to the proximity of the physical mass of H to the minimum value 1.013 u shown in Fig. 4(b).

The same three quasiresonant mechanisms were found for $D_2 + D_2$ and HD + HD collisions. Results are shown for the QRRR mechanism in Figs. 5 and 6 for the initial (v, j; $v - 1$, $j + 2$) states. For $D_2 + D_2$ collisions, the QRRR process dominates for all v, transferring the molecules to (v, $j + 2$; $v - 1$, j) final states. For HD + HD collisions, the QRRR mechanism is suppressed at low v due to competition with efficient $\Delta j = -1$ transitions. In both cases, a zero-energy resonance is found; however, due to the larger reduced mass for these colliders, the zero-energy resonances occur at higher values of v (between $v = 8$ and $v = 9$ for HD self-collisions and between $v = 12$ and $v = 13$ for D_2 self-collisions). Similar results are found for the QRVV and QRVR mechanisms.

Previous studies have demonstrated that quasiresonant mechanisms are not very sensitive to details of the PES for H_2 self-collisions [28]. Ruiz *et al.* have recently examined similar quasiresonant processes classically with a model H_2-H_2 potential [14]. They found that the process could be characterized in terms of changes in classical action, though changes in v and j predicted classically are significantly less than one quantum [14]. This is consistent with previous findings on atom-diatom systems [13]. While the mechanism is demonstrated here for nonreactive collisions of hydrogen isotopologs, it may also apply to other nonreactive systems. However, it is not clear whether

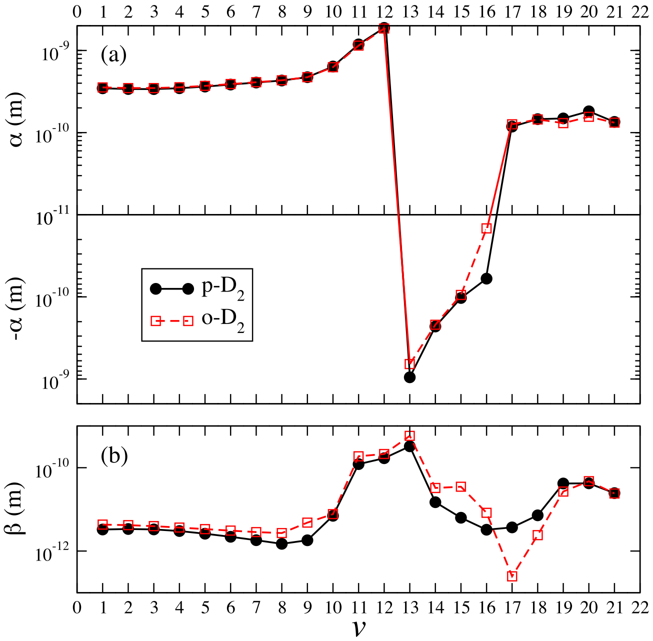

FIG. 5 (color online). Same as Fig. 2 except for $D_2 + D_2$ collisions. Para-D_2, $j = 1$; ortho-D_2, $j = 0$. Similar to $H_2 + H_2$, the value of β is dominated by QRRR transitions to (v, $j + 2$; $v - 1$, j) for all v, but the zero-energy resonance is pushed to a higher value.

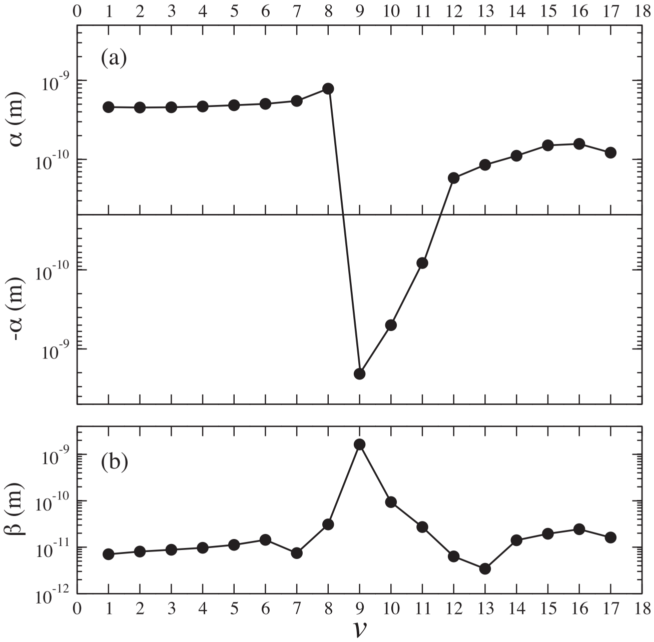

FIG. 6. Same as Fig. 2 except for HD + HD collisions for initial state (v, 0; $v - 1$, 2). The value of β is dominated by QRRR transitions to (v, 2; $v - 1$, 0) for large v, and the zero-energy resonance is located between that of the $H_2 + H_2$ and $D_2 + D_2$ cases.

the effect persists for reactive systems. The location of s-wave zero-energy resonances, which is probably more sensitive to the fine details of the PES, as illustrated by Fig. 4, offers a novel control parameter which could be used to constrain the PES or to tune the quasiresonant mechanisms for even greater efficiency and specificity. For systems containing an initial distribution of vibrationally excited states, e.g., one produced by a typical photoassociation scheme [35], vibrational relaxation may occur primarily through a competition of the three quasiresonant mechanisms.

Support is acknowledged from NASA Grants No. NNX07AP12G and No. NNX12AF42G (B. Y., P. C. S.), NSF Grants No. PHY-0854838 and No. PHY-1203228 (R. C. F.), and NSF Grants No. PHY-0855470 and No. PHY-1205838 (S. F. S., N. B.).

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