Quantum dynamics of rovibrational transitions in H₂-H₂ collisions: Internal energy and rotational angular momentum conservation effects

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We present a full dimensional quantum mechanical treatment of collisions between two H_2 molecules over a wide range of energies. Elastic and state-to-state inelastic cross sections for ortho- H_2 + para- H_2 and ortho- H_2 + ortho- H_2 collisions have been computed for different initial rovibrational levels of the molecules. For rovibrationally excited molecules, it has been found that state-to-state transitions are highly specific. Inelastic collisions that conserve the total rotational angular momentum of the diatoms and that involve small changes in the internal energy are found to be highly efficient. The effectiveness of these quasiresonant processes increases with decreasing collisions between ortho- and para- H_2 molecules for which rotational energy exchange is forbidden, the quasiresonant mechanism involves a purely vibrational energy transfer albeit with less efficiency. When inelastic collisions are dominated by a quasiresonant transition calculations using a reduced basis set involving only the quasiresonant channels yield nearly identical results as the full basis set calculation leading to dramatic savings in computational cost. © 2011 American Institute of Physics. [doi:10.1063/1.3595134]

I. INTRODUCTION

Ever since the first creation of Bose-Einstein condensates (BECs) of alkali metal atoms in 1995 (Ref. 1) experimental and theoretical studies of cold and ultracold molecules have become a topic of intense activity. While direct laser cooling of molecules has proven to be difficult due to their complex internal level structure, photoassociation of ultracold atoms² and methods based on Stark deceleration³ and buffer gas slowing⁴ have enabled the possibility of cooling and trapping a wide variety of molecular species. Novel techniques, such as the Feshbach resonance method,⁵ have enabled the creation of molecular BECs and paved the way for possible control of chemical reaction pathways in ultracold dilute gases.⁶ All these efforts have led to much interest in atomic and molecular collisions at cold and ultracold temperatures. Recent calculations⁷⁻¹⁰ and experiments¹¹⁻¹⁴ on alkali metal systems have indicated that electric and magnetic fields, and optical lattices can be used to tune and modify chemical reaction rates at ultracold temperatures. Electric and magnetic fields and optical lattices can also be used to control interaction and spatial alignment of polar molecules, and application of these techniques to quantum computing and quantum information science is actively being pursued.^{15–18}

The large de Broglie wavelengths characteristic of ultracold collisions lead to interesting phenomena and quantum threshold effects that are absent in thermal energy collisions. Elastic (EL) and inelastic (IN) cross sections may show resonances corresponding to decay of quasibound levels of the interaction potential.^{19,20} The long collision times in cold collisions can quite often exceed the molecular rotational period and the energy exchange among the different degrees of freedom can be more efficient for selected transitions.^{21–23} Highly efficient and selective quasiresonant energy transfer mechanisms have been identified in atom-diatom and diatom-diatom collisions, and it has been found that these processes become more dominant at small incident energies. Such quasiresonant processes have been the topic of a number of studies on vibrational and rotational transitions in atom-diatom systems^{21,22} and more recently in diatom-diatom collisions.²³

While current research on cold and ultracold molecules is motivated in part by applications in areas, such as quantum control of atomic and molecular motion, quantum computing, coherent chemistry, and high resolution spectroscopy, cold molecules also provide a unique opportunity to investigate molecular collisions and mechanisms of energy transfer in an extremely important but rather less explored regime

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that lies between the ultracold (<mK) and temperatures typically accessible in supersonic expansion ($\sim 2-50$ K). The interaction potential between many neutral molecules exhibits a van der Waals well that is typically about 10-100 K deep. In many cases, the well supports bound and quasibound levels that are held by a fraction of a Kelvin to tens of Kelvin. At collision energies that lie in the mK to values comparable to the magnitude of the van der Waals interaction potential, scattering cross sections often exhibit sharp features that are signatures of quasibound states of the van der Waals potential. They may occur from a combination of shape and Feshbach resonances and can significantly modify the probabilities for vibrational and rotational transitions at low temperatures. The importance of orbiting resonances in molecular collisions in this energy regime has been the topic of a recent spotlight article²⁴ and such studies offer a sensitive probe to test the accuracies of potential energy surfaces(PESs).

An accurate calculation of low temperature rate coefficients for molecular collisions should include an accurate treatment of scattering dynamics in this regime. This is particularly important for processes relevant to astrophysical environments, where temperatures as low as 3 K are possible. Moreover, to determine thermally averaged rate coefficients at temperatures near 1 K, cross sections at energies as low as a few mK may be needed in evaluating the integral over the Boltzmann distribution.

Until recently, most theoretical studies of cold molecular collisions have focused on atom-diatom systems. While such calculations can be routinely performed for collisions of rare-gas atoms with light molecules, they become computationally challenging for systems involving heavy diatomics, open shell molecules, and systems with rearrangement channels where reactive scattering is present.²⁵ Diatom-diatom collisions are also challenging due to their increased number of asymptotic channels and higher dimensionality. Because H₂-H₂ is the simplest neutral diatom-diatom system, it has been used as a benchmark to compute interaction potentials for tetratomic systems and also as a test case for developing reliable quantum scattering formalisms for diatom-diatom collisions. Given the importance of molecular hydrogen in the interstellar medium, H2-H2 collisions have also been the topic of a large number of theoretical calculations of state-resolved cross sections and rate coefficients.²⁶⁻³¹ These calculations have largely been carried out at elevated temperatures. Unique aspects of collisions at low energies, or collisions where the vibrational coordinates of both H2 molecules are explicitly included, have not been considered until fairly recently.

Early studies of the H₂-H₂ PES were carried out within the rigid rotor approximation, in which the vibrational motion of each H₂ is kept frozen. As early as 1975, Green investigated pure rotational transitions in H₂-H₂ collisions by quantum close-coupling scattering calculations.³² He compared his results with calculations employing the effective potential approximation and also tested the accuracy of different *ab initio* potential energy surfaces.^{33, 34} Forrey³⁵ reported results of rotational transitions in para-H₂ + para-H₂ collisions at cold and thermal energies using the rigid rotor PES of Zarur and Rabitz.³⁶ Maté *et al.*³⁷ carried out measurements of rotational excitation in collisions between two ground state para-H2 molecules and reported rate coefficients for temperatures between 2 and 110 K. They found generally good agreement between their measured data and results of their own close-coupling calculations using the rigid rotor H₂-H₂ PES of Diep and Johnson (DJ).³⁸ Lee et al.³⁹ investigated rotational energy transfer in collisions between two para-H₂ molecules using the DJ and a newer full-dimensional PES calculated by Boothroyd, Martin, Keogh, and Peterson (BMKP).⁴⁰ Pogrebnya and Clary⁴¹ and Pogrebnya et al.⁴² employed the BMKP and the Schwenke PES (Ref. 43) to compute vibrational relaxation in collisions between para-H₂ within the centrifugal-decoupling or coupled-states (CS) approximation. They also reported rate coefficients for ortho- H_2 + para- H_2 collisions at thermal energies. Quéméner et al.²³ and Quéméner and Balakrishnan⁴⁴ reported results on the BMKP PES for rotational and vibrational transitions in para-H₂ at ultracold and thermal energies. In these calculations, all internal degrees of freedom involved were treated quantum mechanically, and no angular momentum decoupling approximation was invoked. Recently, Hinde reported a full-dimensional PES for the H₂-H₂ system,⁴⁵ that accurately reproduced energy levels of H₂-D₂ and D₂-D₂ van der Waals complexes. Within the same formalism of Ref. 23, Balakrishnan et al.⁴⁶ presented rovibrational relaxation rate coefficients for para-H2-para-H2 collisions on the Hinde PES, and found that it yields vibrational relaxation rate coefficients for $H_2(v = 1)$ in collisions with $H_2(v = 0)$ in close agreement with experimental data. Indeed, the agreement was found to be better than any previous calculations of vibrational relaxation of $H_2(v = 1)$ by collisions with $H_2(v = 0)$.

All of the studies described above have used the solution of the time-independent Schrödinger equation. Timedependent approaches have also been successfully employed in describing H₂-H₂ collisions.^{47,48} Lin and Guo⁴⁹ computed rotational excitation cross sections in collisions between two ground state para-H₂ molecules using two different full dimensional PESs, the BMKP surface and that of Aguado et al.⁵⁰ They employed a wave packet approach based on the Chebyshev polynomial expansion of the evolution operator and within the CS approximation. Later, they extended their work to rovibrational transitions and reported rate coefficients for vibrational relaxation of $H_2(v = 1)$ by collisions with $H_2(v = 0)$.⁵¹ Using the multiconfiguration timedependent Hartree (MCTDH) algorithm, Gatti et al.⁵² and Otto et al.^{47,48} reported rotational excitation cross sections for para- H_2 +para- H_2 collisions employing the BMKP PES. Panda et al.⁵³ subsequently extended these calculations to rovibrational transitions in ortho-para collisions.

While there is an extensive literature on H_2 - H_2 collisions using different PESs and dynamical approximations, with a few exceptions, the majority of studies have focused on para- H_2 molecules in the thermal regime. Data on ortho- H_2 +ortho- H_2 collisions and ortho-para collisions are relatively sparse and most of these studies have either used the rigid rotor approximation or the coupled states approximation for the full-dimensional calculations.^{41,51} While the calculations of Flower³¹ used the full close-coupling method, his rate coefficient calculations were restricted to temperatures of 300 K and 500 K. Furthermore, Flower adopted an asymmetric basis set for the target and perturber molecule with v = 0, j = (1, 3, 5, 7, 9, 11), and v = 1, j = (1, 3, 5, 7) for the target H₂, while only the v = 0 with j = (1, 3, 5) levels have been included for the perturber H₂ molecule. This restriction is lifted in the present work for ortho-ortho collisions and we use identical basis sets for both molecules. In addition, we present results for ortho-ortho and ortho-para collisions in the cold and ultra-cold regimes, and for both cases we use the full close-coupling approach with no angular momentum decoupling approximations. The recently reported high accuracy H₂-H₂ PES of Hinde is employed. We show that rotational and vibrational relaxation rate coefficients are strongly influenced by energy and angular momentum gaps. In accordance with our previous findings on para-H₂ collisions, rovibrational transitions that conserve the total internal rotational angular momentum and that nearly conserve the internal energy are dominant while others are suppressed. In collisions involving initial states for which internal energy and internal rotational angular momentum gaps cannot be simultaneously minimized, vibrational relaxation is found to be driven by the angular dependence of the interaction potential. We show that rate coefficients for vibrational relaxation of ortho- $H_2(v = 1)$ in collisions with ground vibrational state ortho-H₂ molecules obtained from our calculations are generally in reasonable agreement with experimental data. The agreement is less satisfactory compared to that of para-H₂ case,⁴⁶ but still better than previous calculations using BMKP or BMKPE PESs. Unfortunately, the only available measurement below a temperature of 300 K is that of Audibert et al. which was performed in 1975. We believe that for benchmarking the results of full close-coupling calculations obtained using highly accurate interaction potentials, modern measurements would be extremely valuable and we hope the present study will motivate such experiments.

II. THEORY

We present here a brief account of the scattering formalism of two ${}^{1}\Sigma$ diatomic molecules. A more detailed discussion can be found in the original papers of Takayanagi,⁵⁴ Green,³² Alexander and DePristo,⁵⁵ and Zarur and Rabitz.³⁶ As in our previous works,^{23,44} we use the close coupling scheme in the total angular momentum representation of Arthurs and Dalgarno⁵⁶ to solve the time-independent Schrödinger equation. Atomic units are used throughout, unless otherwise noted.

The Hamiltonian of the system is composed of the Hamiltonians for the two diatoms, with their kinetic energy term $\hat{T}(r)$ and potential energy $\hat{v}(\vec{r})$, combined with the kinetic energy for the relative motion, $\hat{T}(R)$, and the four-particle interaction potential $U(\vec{r}_1, \vec{r}_2, \vec{R})$,

$$\hat{H} = \hat{T}(\vec{R}) + \hat{T}_1(\vec{r}_1) + \hat{T}_2(\vec{r}_2) + \hat{v}_1(\vec{r}_1) + \hat{v}_2(\vec{r}_2) + U(\vec{r}_1, \vec{r}_2, \vec{R}),$$
(1)

where (see Fig. 1), \vec{r}_1 and \vec{r}_2 are the vectors joining the two nuclei in each diatomic molecule, and \vec{R} represents the vector joining the center of masses of the diatomic pairs. The



FIG. 1. Jacobi coordinates for the tetratomic system.

spatial orientation of these vectors is denoted by angles \hat{r}_1 , \hat{r}_2 , and \hat{R} . The angular dependence of the interaction potential is expanded in spherical harmonics,

$$U(\vec{r}_1, \vec{r}_2, \vec{R}) = \sum_{\lambda} A_{\lambda}(r_1, r_2, R) Y_{\lambda}(\hat{r}_1, \hat{r}_2, \hat{R}), \qquad (2)$$

where

$$Y_{\lambda}(\hat{r}_{1}, \hat{r}_{2}, \hat{R}) = \sum_{m_{\lambda}} \langle \lambda_{1} m_{\lambda_{1}} \lambda_{2} m_{\lambda_{2}} | \lambda_{12} m_{\lambda_{12}} \rangle$$
$$\times Y_{\lambda_{1}, m_{\lambda_{1}}}(\hat{r}_{1}) Y_{\lambda_{2}, m_{\lambda_{2}}}(\hat{r}_{2}) Y^{*}_{\lambda_{12}, m_{\lambda_{12}}}(\hat{R}), \quad (3)$$

with $\lambda \equiv \lambda_1 \lambda_2 \lambda_{12}$ and $m_{\lambda} \equiv m_{\lambda_1} m_{\lambda_2} m_{\lambda_{12}}$. The quantity in angular brackets, $\langle \lambda_1 m_{\lambda_1} \lambda_2 m_{\lambda_2} | \lambda_{12} m_{\lambda_{12}} \rangle$, represents a Clebsch-Gordon coefficient. The total wave function of the system is expanded in a basis set of the combined asymptotic rovibrational wave functions of the two molecules,

$$\Psi(\vec{r}_1, \vec{r}_2, \hat{R}) = \frac{1}{R} \sum_{vjlJM} F_{vjl}^{JM\epsilon_l}(R) \Phi_{vjl}^{JM\epsilon_l}(\vec{r}_1, \vec{r}_2, \hat{R}), \quad (4)$$

where *J* is the total angular momentum quantum number (which is conserved in the collision) and *M* its projection on the space fixed *z* axis. Vibrational and rotational quantum numbers of the two molecules are represented by $v \equiv v_1v_2$ and $j \equiv j_1 j_2 j_{12}$, where j_{12} is the total rotational angular momentum quantum number of the two molecules which takes values from $|j_1 - j_2|$ to $j_1 + j_2$. The index $\epsilon_I = \pm 1$ indicates the parity of the wave function under spatial inversion, and it is given by $\epsilon_I = (-1)^{J+j_1+j_2+l}$. The asymptotic rovibrational wave functions are given by

$$\Phi_{vjl}^{JM\epsilon_{I}}(\vec{r}_{1},\vec{r}_{2},\hat{R}) = \chi_{vj_{1}j_{2}}(r_{1},r_{2})\langle \hat{r}_{1},\hat{r}_{2},\hat{R}|j_{1}j_{2}j_{12}lJM\rangle,$$

where $\chi_{\nu j_1 j_2}(r_1, r_2) \equiv \chi_{\nu_1 j_1}(r_1) \chi_{\nu_2 j_2}(r_2)$ represents the vibrational wave functions of the two molecules. The rotational wave function is given by

$$\langle \hat{r}_{1}, \hat{r}_{2}, \hat{R} | j_{1} j_{2} j_{12} l J M \rangle = \sum_{m_{j} m_{l}} \langle j_{1} m_{j_{1}} j_{2} m_{j_{2}} | j_{12} m_{j_{12}} \rangle \\ \times \langle j_{12} m_{j_{12}} l m_{l} | J M \rangle \\ \times Y_{i_{l} m_{l}}(\hat{r}_{1}) Y_{i_{l} m_{l}}(\hat{r}_{2}) Y_{lm_{l}}(\hat{R}),$$

where $m_j \equiv m_{j_1} m_{j_2} m_{j_{12}}$. The Clebsch-Gordan coefficients arise from the coupling of j_1 and j_2 to yield j_{12} and from the subsequent coupling of j_{12} and l to yield J. The form of the wave function given by Eq. (4) is appropriate for collisions involving distinguishable molecules, e.g., between ortho-H₂ and para-H₂. For indistinguishable molecules, as in ortho-H₂+ortho-H₂ or para-H₂+para-H₂ collisions, properly symmetrized exchange-permutation invariant functions need to be constructed,

$$\Phi_{vjl}^{JM\epsilon_l\epsilon_P}(\vec{r}_1, \vec{r}_2, \hat{R})$$

= $\Delta_{vj_1j_2} \Big[\Phi_{vjl}^{JM\epsilon_l} + \epsilon_P (-1)^{j_1 + j_2 + j_{12} + l} \Phi_{\tilde{v}\tilde{j}l}^{JM\epsilon_l} \Big]$

where $\Delta_{vj_1j_2} = [2(1 + \delta_{v_1v_2}\delta_{j_1j_2})]^{-1/2}, \bar{v} = v_2v_1, \bar{j} = j_2j_1j_{12},$ and $\epsilon_P = \pm 1$.

Substitution of Eq. (4) into the time-independent Schrödinger equation leads to a set of coupled equations

$$\left\{ -\frac{1}{2\mu} \frac{d^2}{dR^2} + \frac{l(l+1)}{2\mu R^2} + \varepsilon_{\nu j} - E \right\} F_{\nu j l}^{JM\epsilon_l(\epsilon_P)}(R) + \sum_{\nu' j' l'} U_{\nu j l, \nu' j' l'}^{JM\epsilon_l(\epsilon_P)}(R) F_{\nu' j' l'}^{JM\epsilon_l(\epsilon_P)}(R) = 0, \quad (5)$$

in which μ is the reduced mass of the molecule-molecule system, and the collision energy for each channel is given by the difference between the total energy E and the threshold energy ε_{vj} of that channel. The superscripts denote the good quantum numbers, and the molecule permutation symmetry ϵ_P is present only if the molecules are indistinguishable. $U_{vjl,v'j'l'}^{JM\epsilon_l(\epsilon_P)}(R)$ represents the matrix elements of the interaction potential between the asymptotic rovibrational wave functions $\Phi_{vjl}^{JM\epsilon_l\epsilon_P}(\vec{r}_1, \vec{r}_2, \hat{R})$. Explicit expressions for $U_{vjl,v'j'l'}^{JM\epsilon_l(\epsilon_P)}(R)$ for both distinguishable and indistinguishable cases are given in Ref. 44.

At sufficiently large values of R asymptotic boundary conditions are applied to extract the scattering matrix S from which state-to-state cross sections are computed. In the case of indistinguishable molecules, the state-to-state cross sections need to be statistically weighted by the exchange symmetry terms in order to correctly account for the nuclear-spin permutation,

$$\sigma_{v_1 j_1 v_2 j_2 \to v'_1 j'_1 v'_2 j'_2}(E_c) = W^+ \sigma^{\varepsilon_P = +1} + W^- \sigma^{\varepsilon_P = -1},$$

where

$$\sigma^{\varepsilon_{P}} = \frac{\pi (1 + \delta_{\nu_{1}\nu_{2}} \delta_{j_{1}j_{2}})(1 + \delta_{\nu'_{1}\nu'_{2}} \delta_{j'_{1}j'_{2}})}{(2j_{1} + 1)(2j_{2} + 1)2\mu E_{c}} \times \sum_{j_{12}j'_{12}l'J\varepsilon_{l}} (2J + 1)|\delta_{\nu_{1}\nu_{2}} \delta_{\nu'_{1}\nu'_{2}} \delta_{j_{1}j_{2}} \delta_{j'_{1}j'_{2}} - S^{J\varepsilon_{l}\varepsilon_{P}}_{\nu_{1}j_{1}\nu_{2}j_{2}j_{12},\nu'_{1}j'_{1}\nu'_{2}j'_{2}j'_{2}}(E_{c})|^{2}.$$
(6)

The collision energy E_c is specified relative to the channel energy and it is given by $E_c = E - \varepsilon_{v_1j_1} - \varepsilon_{v_2j_2}$. For collisions between para-H₂ molecules, $W^+ = 1$ and $W^- = 0$ and for ortho-H₂ collisions, $W^+ = 2/3$ and $W^- = 1/3$. For the distinguishable case, the state-to-state cross section is given by the usual formula

$$\sigma_{\nu_{1}j_{1}\nu_{2}j_{2} \to \nu_{1}'j_{1}'\nu_{2}'j_{2}'}(E_{c}) = \frac{\pi}{(2j_{1}+1)(2j_{2}+1)2\mu E_{c}} \times \sum_{j_{12}j_{12}'ll'J\varepsilon_{I}} (2J+1)|\delta_{\nu_{1}\nu_{2}}\delta_{\nu_{1}'\nu_{2}'}\delta_{j_{1}j_{2}}\delta_{j_{1}'j_{2}'} -S_{\nu_{1}j_{1}\nu_{2}j_{2}j_{12},\nu_{1}'j_{1}'\nu_{2}'j_{2}'j_{12}'}(E_{c})|^{2}.$$
(7)

Calculations are carried out separately for the two inversion parities and the final cross sections are obtained by adding the two contributions.

III. RESULTS

A. Computational details

In our previous studies we have focused on collision dynamics of two para-H₂ molecules treating them as indistinguishable molecules. For para-H₂ only one exchange symmetry contributes, and the calculations are generally computationally less demanding than the ortho-H₂ case for which both exchange symmetries need to be included. For the ortho-para case no exchange symmetries are present and the full distinguishable basis must be employed. This leads to a significantly larger basis set making the calculations computationally more challenging.

Here, we present collision dynamics of two indistinguishable ortho-H₂ molecules and also collisions of ortho-H₂ and para-H₂ molecules. The calculations were performed using a modified version of the quantum scattering code TwoBC (Ref. 57) based on the formalism described in Sec. II. In the case of indistinguishable molecules, the rovibrational quantum numbers that define a state $|v, j\rangle$ obey the "well ordered states classification,"^{32,54,55} in which $v_1 > v_2$ when $v_1 \neq v_2$, or $j_1 \geq j_2$ when $v_1 = v_2$. This ordering scheme avoids double-counting and equivalent molecular states are combined into a single state: i.e., $|v_1, j_1, v_2, j_2\rangle \equiv |v_2, j_2, v_1, j_1\rangle$. In non-reactive scattering, in which permutation of the H-atoms between the two H₂ molecules does not occur, this representation of the wave function is unique before and after the collision.

The number of states included in the expansion of the wave function has been determined based on a series of convergence tests. The final basis set employed reflects a compromise between accuracy and computational cost. The truncation of the basis set was guided by an analysis of the effective potential,

$$V_{eff}^{J}(R) = \varepsilon_{vj} + \mathcal{U}_{vjl,vjl}^{JM\varepsilon_{I}\varepsilon_{P}}(R) + \frac{l(l+1)}{2\mu R^{2}}.$$
 (8)

The first term is the energy of the combined molecular state $|v_1, j_1, v_2, j_2\rangle$ obtained by adding the asymptotic energies of $|v_1, j_1\rangle$ and $|v_2, j_2\rangle$. The second term is the diagonal element of the diabatic potential energy coupling matrix and the third term is the centrifugal potential for a given value of the orbital angular momentum quantum number *l*. At large intermolecular separations, the energies of the different channels that correspond to the same combined molecular state (CMS) converge to its asymptotic value. Table I lists energies of CMSs of

TABLE I. Rovibrational energies of various combined molecular states of the two ortho- H_2 molecules included in the calculations. Energies are relative to the bottom of the H_2 potential and the zero-point energy of the orthoortho complex in this case is 4595.263 cm⁻¹. Some of the channels that are excluded in the calculations by imposing a cut-off energy are also shown.

<i>v</i> ₁	j_1	v_2	j_2	$\varepsilon_{vj} \ (\mathrm{cm}^{-1})$	ε_{vj} (K)	v_1	j_1	v_2	j_2	$\varepsilon_{vj} \ (\mathrm{cm}^{-1})$	ε_{vj} (K)
0	1	0	1	4595.263	6617.179	1	5	0	5	11910.837	17151.605
0	3	0	1	5182.011	7462.096	1	7	0	3	12249.645	17639.489
0	3	0	3	5768.759	8307.013	1	3	0	7	12375.392	17820.564
0	5	0	1	6216.196	8951.322	0	9	0	7	12544.120	18063.533
0	5	0	3	6802.944	9796.239	1	1	1	1	12905.617	18584.088
0	7	0	1	7662.828	11034.472	1	7	0	5	13283.830	19128.715
0	5	0	5	7837.129	11285.466	1	5	0	7	13357.469	19234.755
0	3	0	7	8249.576	11879.389	1	3	1	1	13463.004	19386.726
0	1	1	1	8750.440	12600.634	1	1	0	9	13631.732	19629.694
0	7	0	5	9283.761	13368.616	cut off					
1	3	0	1	9307.827	13403.271	1	3	1	3	14020.392	20189.364
1	1	0	3	9337.188	13445.551	1	3	0	9	14189.120	20432.332
0	9	0	1	9476.555	13646.239	0	9	0	9	14357.848	20675.301
1	3	0	3	9894.576	14248.189	1	5	1	1	14445.081	20800.917
0	9	0	3	10063.304	14491.158	1	7	0	7	14730.461	21211.864
1	5	0	1	10289.904	14817.462	1	5	1	3	15002.468	21603.554
1	1	1	5	10371.373	14934.777	1	5	0	9	15171.196	21846.522
0	7	0	7	10730.393	15451.766	1	1	1	7	15818.073	22778.025
1	5	0	3	10876.652	15662.379	1	5	1	5	15984.545	23017.745
1	3	0	5	10928.760	15737.414	1	7	1	3	16375.461	23580.664
0	9	0	5	11097.488	15980.383	1	7	0	9	16544.189	23823.632
1	7	0	1	11662.896	16794.570	1	7	1	5	17357.537	24994.853
1	1	0	7	11818.005	17017.927	1	7	1	7	18730.530	26971.963

two ortho- H_2 molecules that are included in the calculations and those of nearby closed channels that are excluded.

An energy cut-off of $14\,000\,\mathrm{cm}^{-1}$, $\sim 20\,140\,\mathrm{K}$, was introduced to limit the number of states in the basis set. Without this limit calculations would have become prohibitively expensive for high energies and high J values. The final basis set for ortho-ortho calculations included $j_{max} = 9$ for v = 0and $j_{\text{max}} = 7$ for v = 1 for both molecules. This means that for the ground vibrational level, we included rotational levels j = 1, 3, 5, 7, and 9, and for the first excited vibrational level, rotational levels i = 1, 3, 5, and 7. For the initial states considered in this study, this choice of the basis set is found to yield results converged to better than 5%. For the orthopara case, an equivalent basis set was adopted for ortho-H₂, while for the para counterpart we used v = 0, $j_{max} = 8$, and for v = 1, $j_{max} = 6$ based on previous calculations of para-H₂-para-H₂ collisions.⁴⁶ The basis set includes 32 combined molecular states for the ortho-ortho case and 70 for the orthopara case.

The log-derivative matrix propagation method of Johnson⁵⁸ and Manolopoulos⁵⁹ was used to integrate the coupled equations (5) from $R_{min} = 3 a_0$ to $R_{max} = 53 a_0$ at which asymptotic boundary conditions are applied to evaluate the scattering matrix. To keep the computational cost reasonable, the ortho-para results were obtained for collision energies below 100 K which required J up to 10 for yielding converged cross sections. The ortho-ortho calculations for vibrational self-relaxation of H₂(v = 1) included collision energies up to 10 000 K and J values up to 85. As an example of computational cost, it took about 1120 h of CPU

time in an AMD Opteron cluster for the ortho-para case 1001 and for positive inversion parity. For the ortho-ortho case 1103 and for positive inversion parity it took 304 h for energies up to 100 K and 3500 h from 100 K to 10 000 K. Overall, the production calculations required over 50 000 CPU h in Opteron clusters and quad core Mac OSX workstations. The high energy range of the orthopara calculations involved nearly 3000 coupled-channel equations.

For ortho-H₂ collisions, three different initial states have been chosen: $H_2(v = 1, j = 1) + H_2(v = 0, j = 1)$, $H_2(v = 1, j = 1) + H_2(v = 0, j = 3)$, and $H_2(v = 1, j = 3)$ + H₂(v = 0, j = 1), respectively, 1101, 1103, and 1301. For the ortho-para case, we focused on 1001 and 1201. Figure 2 displays the elastic cross sections for all five initial states at collision energies ranging from 0.1 mK to 100 K. Except for the resonant features, which will be addressed in more detail later on, the cross sections depict similar energy dependence and comparable values in the entire energy range spanning six orders of magnitude. This is in agreement with our previous study of para-H₂ collisions, where it has been shown that the elastic cross sections are largely insensitive to the initial rovibrational levels of the two H₂ molecules except when quantum statistics effects are present.²³ The zeroenergy limits of the cross sections are 374.7×10^{-16} cm² for 1101, 370.9×10^{-16} cm² for 1103, 369.0×10^{-16} cm² for 1301, 386.7×10^{-16} cm² for 1001, and 371.9×10^{-16} cm² for 1201.

In our previous study of para- H_2 collisions, it has been found that inelastic collisions that conserve the total ro-



FIG. 2. Elastic cross sections for initial combined molecular states 1001, 1101, 1103, 1201, and 1301 as functions of the incident kinetic energy.

tational angular momentum and that nearly conserve the internal energy of the two molecules are highly efficient and specific.²³ This has been analyzed in detail for the initial state 1002, which preferentially leads to the 1200 final state. The energy transfer occurs primarily through a swapping of rotational quantum numbers between the two molecules. Here, we will examine if this persists for ortho-H₂ collisions and how it is modified for the ortho-para case for which rotational energy exchange is forbidden for inelastic collisions.

B. Ortho-ortho calculations

Figure 3 shows state-to-state rovibrational transition cross sections for 1101 collisions. Although exchange of rotational quantum number between the two molecules is allowed in this case, it corresponds to an elastic process because the molecules are indistinguishable. The main contribution to the total inelastic cross section arises from the process $1101 \rightarrow 0505$, which has the second least energy gap, of about 1314 K. Pure vibrational relaxation of the v = 1molecule is found to be the next dominant transition, even though the energy gap for this transition is the largest among



FIG. 3. Total IN and state-to-state cross sections as functions of the incident kinetic energy for $H_2(\nu = 1, j = 1) + H_2(\nu = 0, j = 1)$ collisions.

TABLE II. Percentage contributions of selected final states to the total inelastic cross section for the 1101 initial state from calculations assuming the molecules to be distinguishable (upper panel) and indistinguishable (lower panel).

Final CMS	10 ⁻⁶ K	$10^{-3} { m K}$	1 K	10 K	100 K
Distinguishable					
01-11	99.66	99.99	99.99	99.99	99.99
05-05	0.0717	0.0023	4.3×10^{-6}	3×10^{-5}	3.12×10^{-4}
01-01	0.0216	0.0007	1.6×10^{-6}	7.13×10^{-6}	5.98×10^{-5}
Indistinguishable					
01-11					
05-05	45.24	45.34	46.74	63.72	55.74
01-01	16.5	16.54	18.47	22.53	22.33

all the exoergic inelastic transitions, 5978.34 K. Table II presents the percentage contributions of selected inelastic transitions to the total inelastic cross section at five different collision energies, 10^{-6} , 10^{-3} , 1, 10, and 100 K. Interestingly, when we treat these molecules as distinguishable, disregarding the fact that they both have the same nuclear spin, it is found that vibrational exchange becomes the dominant inelastic transition. This can be explained by recalling that when the molecules are treated as indistinguishable we have $|v_1, j_1, v_2, j_2\rangle \equiv |v_2, j_2, v_1, j_1\rangle$; therefore, vibrational exchange is being incorporated into the elastic cross section. Treating the molecules as distinguishable separates these two channels and one can identify their individual contributions. Furthermore, since the energy gap between the initial, $|1, 1, 0, 1\rangle$, and final, $|0, 1, 1, 1\rangle$, states is zero, and the total internal rotational angular momentum is conserved, it is expected that this would be the dominant inelastic process. Analogous to the quasiresonant rotation-rotation (QRRR) transfer as in 1002 to 1200 case, this may be termed as resonant vibration-vibration (RVV) transfer, for the process is exactly resonant.

Elastic and total inelastic cross sections for the 1103 initial state are shown in the upper panel of Fig. 4. For energies below 10^{-2} K, the elastic cross section attains finite values while the inelastic cross section diverges inversely as the incident velocity, in accordance with the Wigner threshold laws.⁶⁰ At incident collision energies below 10^{-4} K, the inelastic cross section exceeds the elastic cross section which is also a consequence of Wigner's threshold law. To demonstrate the dominance of QRRR transition in this case, we display selected inelastic cross sections in the middle and bottom panels of Fig. 4. The middle panel shows some rovibrational transitions along with the total inelastic cross section. It is seen that the main contribution to the inelastic process comes from the $1103 \rightarrow 1301$ transition. This process involves the exchange of two quanta of rotational energy between the two hydrogen molecules and the least energy gap (42.24 K). Two other transitions, with cross sections a few orders of magnitude smaller than that of the dominant inelastic process, correspond to $1103 \rightarrow 1101$ (pure rotational quenching) and $1103 \rightarrow 0705$. A comparative analysis of them reveals that even though the energy gap is smaller, 76.86 K for the latter compared to 844.14 K of the former, minimization of inCross section (10^{-16} cm^2)

Inelastic cross section (10^{-16} cm^2)





FIG. 4. EL, total IN, and state-to-state cross sections as functions of the incident kinetic energy for 1103 collisions. Upper panel: Elastic and total inelastic cross section; middle panel: Total inelastic and dominant inelastic cross sections along with a few less prominent state-to-state cross sections; lower panel: State-to-state cross sections that make negligible contributions to the total inelastic cross section.

ternal angular momentum change dominates internal energy conservation, suppressing an exponential-energy-gap-lawtype behavior seen for pure rotational transitions in several atom-molecule systems.⁶¹ The lower panel of Fig. 4 depicts all the remaining state resolved inelastic cross sections, which make negligible contribution to the total inelastic cross section. Results show that depending on the combination of initial rovibrational quantum numbers of the



FIG. 5. Total IN and state-to-state cross sections as functions of the incident kinetic energy for $H_2(\nu = 1, j = 3) + H_2(\nu = 0, j = 1)$ collisions. The upper panel shows the total inelastic and some dominant state-to-state cross sections while the lower panel shows the negligible contribution from many inelastic channels.

colliding molecules, energy and angular momentum gaps dictate the magnitude of state-to-state cross sections. The results obtained by treating the molecules as distinguishable confirm that the rotational exchange dominates all other inelastic processes. In this case, vibrational exchange accounts for less than 1% of the total inelastic cross section. This is not surprising because the interaction potential is more sensitive to the orientation of the H₂ molecules than the H-H bond distance.

Results for 1301 collisions are shown in Fig. 5. The upper panel displays the total inelastic and a few selected stateto-state cross sections. The most interesting feature appears to be the interplay among the two main inelastic channels, $1301 \rightarrow 1101$ and $1301 \rightarrow 1103$. As in the previous cases, conservation of internal angular momentum (and to a lesser extent, conservation of internal energy) seems to be what drives the transitions. For energies below the opening of the 1103 channel (see Table I), the inelastic process is mostly driven by the quenching of the rotationally excited molecule leading to the 1101 product channel. At a collision energy of about 42.24 K, at which the 1103 channel becomes energetically open, the inelastic cross section becomes dominated by the 1103 final state. Treating the molecules as distinguishable reveals that at an incident energy of 1 K vibrational and rotational exchange leading to 0113 has the largest contribution (72.18%) while pure rotational quenching leading to 1101 contributes 27.5%. In both 1103 and 1301 collisions, when the QRRR mechanism is present, vibrational relaxation is about five orders of magnitude less efficient than the dominant inelastic transition.

At energies above 100 K, a few more channels become energetically open for all the ortho-ortho cases presented here. Selected channels are shown in Figs. 3-5. The dominant process for all cases is the rotational excitation of the H₂ molecule in its vibrational ground state, the process that has the smallest angular momentum gap among the newly open channels.

1. Vibrational relaxation rate coefficients

Rate coefficients for vibrational relaxation of $H_2(v = 1)$ were calculated for the ortho-ortho case by weighting the vibrational de-excitation rate coefficients of 1101, 1103, and 1301 according to³¹

$$R_{1\to0}(T) = \sum_{v_1'j_1'v_2'j_2'} n(v_1j_1)n(v_2j_2) \\ \times R(v_1j_1v_2j_2 \to v_1'j_1'v_2'j_2')$$
(9)

in which the sum runs over the final states and

$$n(vj) = \frac{(2j+1)\exp[-\epsilon_{vj}/kT]}{\sum_{vj}(2j+1)\exp[-\epsilon_{vj}/kT]},$$
(10)

where k in the Boltzmann constant.

The vibrational relaxation rate coefficients are shown in Fig. 6. The temperature range spans from 1 to 500 K, and the state-to-state rate coefficients $R(v_1 j_1 v_2 j_2 \rightarrow v'_1 j'_1 v'_2 j'_2)$ were obtained from the corresponding cross sections computed for collision energies from 10^{-6} to 10^4 K for the 1101, 1103, 1301 initial CMSs. The upper panel of Fig. 6 displays the vibrational de-excitation rate coefficients for the different initial states, theoretical calculations of Pogrebnya and Clary,⁴¹ as well as the experimental results of Audibert et al.⁶³ Pogrebnya and Clary used the BMKPE PES within the CS approximation. Lin and Guo have reported rate coefficients for ortho-ortho H₂ collisions using the BMKP PES within a time-dependent approach⁵¹ and have found that their results are three to ten times larger than the experimental data. Comparing our results against those of Pogrebnya and Clary reinforces previous findings^{41,46} that the less anisotropic BMKPE PES yields results in better agreement with experiment, and with the Hinde PES employed in our calculations. The lower panel of Fig. 6 presents the thermal averaged vibrational relaxation rate coefficients, $R_{1\to 0}(T)$, experimental results of Audibert et al.63 and theoretical calculations of Flower.³¹ Flower's calculations were carried out on the H₄ PES of Schwenke and with an asymmetric basis set for the two H₂ molecules as discussed earlier. We attribute the difference between ours and Flower's results to his choice of truncated basis set and choice of PES. Our results are higher than the experimental values for temperatures below 200 K, but they slightly underestimate the experimental data at temperatures above 300 K. While inclusion of additional



FIG. 6. Temperature dependence of calculated vibrational relaxation rate constants (solid lines) for ortho-ortho H₂ collisions. The upper panel shows the initial state resolved rate coefficients for 1101, 1103, and 1301 together with the available results of Pogrebnya *et al.*⁴¹ for the 1101 initial state (triangles). The lower panel displays vibrational relaxation rate coefficients averaged over a thermal population of rotational levels in v = 0 and v = 1 evaluated using Eq. (9). Experimental results of Audibert *et al.* (shown in both panels)⁶³ and theoretical results of Flower³¹ are also included for comparison. The rate coefficients for the 1101, 1103, and 1301 initial states in the upper panel, and the averaged vibrational relaxation rate coefficient in the lower panel are provided as supplementary material, see Ref. 62.

rotational levels in the thermal averaging may improve the agreement at higher temperatures, the discrepancy at lower temperatures indicate that a re-evaluation of the experimental data and/or calculations using a more accurate H_2 - H_2 potential are needed. As far as our theoretical results are concerned, the only approximation is the truncation of the basis set which results in less than 5% error.

C. Ortho-para calculations

Figure 7 presents the cross sections for 1201 collisions. The upper panel displays the leading inelastic channels while the middle panel shows the remaining state-to-state cross sections. The lower panel depicts partial cross sections for different values of J and parities, $\varepsilon_I = \pm 1$, to identify the partial wave contribution to the main resonance features in the cross section. The upper panel shows that rotational de-excitation of para-H₂ leading to 1001 is the dominant inelastic process in the entire energy range. Since an ortho-para transition



FIG. 7. Inelastic cross sections as functions of the incident kinetic energy for the 1201 collisions. Upper panel: total inelastic cross section and leading state-to-state cross sections; Middle panel: Cross sections for all other inelastic channels (the legend follows the order of the cross section values at 100 K); Bottom panel: Partial cross sections for different values of J that contribute to the resonance peaks at 0.07 K, 1.2 K, and 18.3 K. The various partial cross sections are labeled by $J\varepsilon_I$.

(nuclear spin interconversion) is not allowed, this process involves minimum change in angular momentum. The energy gap is 484.16 K. The second-most dominant inelastic transition is the exchange of a vibrational quantum between the two H_2 molecules leading to the final state, 0211. This lies about 16.95 K above the initial state, and the sharp rise in the cross section at this value of the collision energy arises from the opening of this channel. Although the process involves simultaneous exchange of a vibrational quantum between the two molecules, it is quite efficient because of the small energy gap



FIG. 8. Inelastic cross sections as functions of the incident kinetic energy for 1001 collisions. The legend follows the decreasing order of the cross section values at 100 K.

and zero angular momentum change. The next leading inelastic channel contributes less than 0.01% to the total inelastic cross section. It involves both vibrational exchange and rotational quenching of the para-H₂ molecule yielding 0011 with an energy gap of 492.67 K. All other inelastic channels make negligible contributions to the total inelastic cross section as shown in the middle panel of Fig. 7. Thus, even though many final states are energetically allowed the total inelastic cross section is dominated by a few channels that involve small energy and angular momentum gaps.

The state-to-state cross sections as a function of the incident kinetic energy show resonant enhancement at energies of about 0.07 K, 1.2 K, and 18.3 K. Since they are present in all state-to-state cross sections it appears that they arise from features in the entrance channel of the interaction potential. The energy spacing between these resonances is very small compared to the energy level separation between different rovibrational levels of the H₂ molecule. Also, the van der Waals well depth of the $H_2 \cdots H_2$ complex is about 57.0 K, much smaller than the energy level separation between the H₂ rovibrational levels. Thus, we rule out the possibility of Feshbach resonances at collision energies depicted in Fig. 7 and attribute the features to orbiting resonances. To identify the partial wave contribution to the resonances we show in the lower panel of Fig. 7 the J-resolved contributions to the total inelastic cross section. Each curve is labeled by $J\varepsilon_I$. The sharp feature at 0.07 K originates solely from l = 2 with J = 2 and $\epsilon_I = -1$. Interestingly, the resonance at 1.2 K and the weak bump near 8 K, appear to include contributions from several J values leading to much broader features compared to the 0.07 K resonance. Using the notation $(l, J\epsilon_I)$, the 1.2 K resonance is dominated by the d-wave scattering partial waves (2,1+), (2,2-), (2,3+), (2,4-), and (2,5+), while f-wave scattering from (3,0+), (3,1-), (3,2+), (3,3-), and (3,4+) is primarily responsible for the 8 K feature. We therefore attribute these features, and similar structures in ortho-ortho scattering, to orbiting resonances. The resonance at 18.3 K, however, is due to the opening of the 1102 channel.

In Fig. 8, we present inelastic cross sections for the initial state 1001 as functions of the incident kinetic energy. It is seen

that the total inelastic cross section is dominated by the final state 0011. Since an ortho-para transition is not allowed, this does not occur through a rotational exchange but through a vibrational transfer between the two molecules. We denote this process as quasi-resonant vibration-vibration (QRVV) transfer. The energy gap is only 8.5 K, the lowest possible in H_2+H_2 collisions and it arises from the centrifugal distortion of the vibrational levels v = 0 and 1 by the j = 1 rotational level. Although the pure vibrational transition $1001 \rightarrow 0001$ also involves no change in the internal angular momentum, it involves a large energy gap of about 6000 K making it about three orders of magnitude less efficient than the near-resonant 1001 to 0011 transition. All other inelastic channels combined contribute less than 0.01% to the total cross section.

In a recent quantum mechanical study of H_2 - H_2 collisions using the MCTDH approach, Panda *et al.*⁵³ have shown that in ortho-para collisions, rotationally elastic transitions are dominated by vibrational exchange as in 1001 to 0011. Though the calculations of Panda *et al.* employed the BMKP and BMKPE PESs the overall findings of their study are in agreement with our results. Since they employed the time-dependent wave packet approach, which is not robust for low



FIG. 9. Comparison between cross sections obtained using the full basis set and a reduced basis set for 1001 collisions. The reduced basis set included only the quasiresonant channels. Upper panel: comparison between EL and total IN cross sections; Lower panel: comparison between the dominant inelastic cross sections.

energy calculations, they focused their studies on collision energies above 0.1 eV (\sim 1200 K). Given the fact that the QRRR and QVVV transitions become more dominant at low energies, the highly specific nature of these transitions shown here are not apparent in their calculations, which concentrated primarily on excitation collisions. To reduce computational effort they performed calculations for selected values of J and used an interpolation scheme to evaluate cross sections for the remaining J values.

We have also performed equivalent calculations for the 1001 case with an extremely reduced basis set, which includes solely the rovibrational states responsible the quasiresonant transition. With this choice only four combined molecular states were included (see Table I), namely: 0001, 0011, 1001, and 1011. As illustrated in Fig. 9, results of this calculation reproduce the full basis set results within 5% or less. Also, no appreciable difference is seen between the elastic cross section calculated with the two basis sets. The smaller basis set leads to dramatic savings (nearly 99%) in computational effort. Our analysis shows that in cases where QRVV or QRRR transitions are present, a very small basis set consisting of only the quasiresonant channels can yield accurate results with very little computational effort. This will allow efficient and routine calculations of collisional parameters in weakly interacting molecule-molecule systems relevant to cold and ultracold collisions.

IV. CONCLUSION

We have carried out explicit quantum calculations of rotational and vibrational energy transfer in collisions between two ortho-H₂ molecules as well as ortho- and para-H₂ molecules in selected initial states. A recently reported full-dimensional H₂-H₂ potential surface by Hinde is employed in the calculations. Results show that both energy and angular momentum considerations play a key role in rovibrational transitions in H₂-H₂ collisions. In particular, inelastic collisions that conserve the total internal rotational angular momentum and that nearly conserve the internal energy of the two molecules are found to be highly efficient and selective, in agreement with previous results on para-H₂ collisions. The selectivity of these quasiresonant rotation-rotation transitions increase with decrease in collision energy. In ortho-para collisions where rotational energy exchange is not allowed, the quasiresonant process occurs through a vibrational quantum exchange. Thus, for 1001 collisions the total inelastic cross section is found to be completely dominated by the 0011 final channel which corresponds to the exchange of a quantum of vibrational energy between the two molecules. This quasiresonant vibration-vibration process dominates all other inelastic de-excitation channels by about four orders of magnitude. However, the magnitude of the QRVV transition is about two orders of magnitude smaller than the 1103 to 1301 QRRR transition. This is attributed to the relatively weak dependence of the intermolecular potential on H-H vibrational coordinate as compared to strong angular anisotropy. Our findings on QRVV transfer in ortho-para collisions are in overall agreement with previous time-dependent calculations of Panda et al. performed at higher energies.

However, our calculations show that the near resonant transitions become highly efficient and selective at low energies. When QRVV/QRRR channels are present, the full basis set can be replaced by a minimal basis set consisting of only the QRVV/QRRR channels leading to dramatic savings in computational effort without compromising the accuracy.

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