Multi-channel distorted-wave Born approximation for rovibrational transition rates in molecular collisions

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ABSTRACT
Modeling protoplanetary disks and other interstellar media that are not in local thermal equilibrium require the knowledge of rovibrational transition rate coefficients of molecules in collision with helium and hydrogen. We present a computational method based on the numerically exact coupled-channel (CC) method for rotational transitions and a multi-channel distorted-wave Born approximation (MC-DWBA) for vibrational transitions to calculate state-to-state rate coefficients. We apply this method to the astrophysically important case of CO$_2$–He collisions, using newly computed ab initio three-dimensional potential energy surfaces for CO$_2$–He with CO$_2$ distorted along the symmetric and asymmetric stretch ($\nu_1$ and $\nu_3$) coordinates. It is shown that the MC-DWBA method is almost as accurate as full CC calculations, but more efficient. We also made computations with the more approximate vibrational coupled-channel rotational infinite-order sudden method but found that this method strongly underestimates the vibrationally inelastic collision cross sections and rate coefficients for both CO$_2$ modes considered.

I. INTRODUCTION

Planet formation is a complicated process that produces a great diversity of planets: gaseous or rocky, with different compositions and different atmospheres. Much effort has been devoted to modeling and understanding this process and how it depends on the compositions of and conditions in protoplanetary disks. Crucial information can be extracted from the rovibrational emission spectra of small molecules, such as CO, CO$_2$, C$_2$H$_2$, CH$_4$, H$_2$O, and HCN, observed by using ground or satellite based telescopes.\textsuperscript{1, 2} Interesting infrared spectra have already been measured by using the Infrared Space Observatory and the Spitzer Space Telescope. Much more detailed data will be provided by using the James Webb Space Telescope (JWST)\textsuperscript{3} because of its higher resolution and wider spectral range. Several of these molecules also occur in the Earth’s atmosphere and in the atmospheres of other (exo)planets. Their rovibrational emission or absorption spectra are a tool to study these atmospheres.\textsuperscript{7}

When the environment of the molecules that emit or absorb infrared radiation is in local thermal equilibrium (LTE), the spectra contain information about the abundance of various types of molecules and about the local temperature. When the radiation originates from non-LTE environments, such as various regions in protoplanetary disks, the spectra contain even more information. It is harder to extract this information, though, because the construction of a full non-LTE model requires solving the master equation of the rovibrational level populations in the molecules whose main ingredients are the Einstein A and B coefficients of spontaneous and stimulated emission and state-to-state collisional transition rate coefficients.\textsuperscript{4, 5} The Einstein A and B coefficients of the various molecules are usually known, but the energy transfer rates in collisions with the most abundant species: electrons, hydrogen atoms and molecules, and helium atoms, are often not available yet. Models developed by astronomers often use values from scaling laws, etc., which are mostly inaccurate.\textsuperscript{3} More accurate values can be obtained from quantum mechanical scattering calculations based on
intermolecular potential surfaces obtained from \textit{ab initio} electronic structure calculations.

A prime molecule in these studies is CO$_2$. It cannot be observed through rotational transitions in the far-infrared and submillimeter regions because of the lack of a permanent dipole moment, but can be observed through its vibrational transitions at near- and mid-infrared wavelengths. It has three vibrational modes: a twofold degenerate bend mode, an asymmetric stretch mode, and a symmetric stretch mode, which is not IR active by itself but becomes observable through a Fermi resonance with the bend overtone. Pioneering work on calculating cross sections and rate coefficients for vibrational transitions in CO$_2$ induced by collisions with rare gas (Rg) atoms was carried out in the 1980s by Clary et al. They used a method called VCC-IOS, a vibrational coupled-channel (CC) method for the vibrations, combined with the infinite-order sudden (IOS) approximation for the rotations, which in one example was tested against the less approximate coupled-state approximation (CSA). Although their CO$_2$-Rg potentials were based on \textit{ab initio} electronic structure calculations, it is nowadays possible to obtain much more accurate and detailed intermolecular potential energy surfaces. Also more accurate calculations of collision cross sections and rate coefficients can now be made with the numerically exact CC method. Clary’s calculations provided the rate coefficients for vibrational transitions without considering specific initial and final rotational states, but the more advanced models currently being developed by astronomers and the availability of JWST data in the near future require rovibrational state-to-state collisional rate coefficients for temperatures ranging between 10 and 1500 K. Full CC calculations are still cumbersome and time-consuming, especially at higher collision energies; here, we show how one can reach the CC level of accuracy with a more efficient procedure. In this procedure, all rotational channels for each vibrational quantum number \( \nu \) are treated with the full CC method, while the smaller couplings between different vibrational states are treated perturbatively with a multi-channel distorted-wave Born approximation (MC-DWBA). The application of this algorithm and its accuracy will be illustrated by considering rovibrational transitions in the symmetric and asymmetric stretch modes of CO$_2$ induced by collisions with He atoms.

Section II describes the basic theory. Section III provides the computational details. The results are presented and discussed in Sec. IV. Finally, Sec. V gives a summary and the conclusions, and the Appendix contains a derivation of the MC-DWBA formulas used.

II. THEORY

The molecule CO$_2$ has three vibrational modes: a twofold degenerate bend mode \( \nu_2 \), a symmetric stretch mode \( \nu_1 \), and an asymmetric stretch mode \( \nu_3 \), with experimental frequencies of 667, 1333, and 2349 cm$^{-1}$, respectively. Here, we consider the two stretch modes \( \nu_1 \) and \( \nu_3 \). The corresponding normal coordinates are conventionally denoted as \( Q_1 \) and \( Q_3 \), respectively. We apply the quantum mechanical coupled-channel method to calculate the cross sections and rate coefficients of the rovibrational transitions in each of these modes for collisions of CO$_2$ with He atoms, and we investigate the applicability of the MC-DWBA. Section II briefly describes the basic theory.

A. Coupled-channel method

We use body-fixed (BF) coordinates to define the geometry of the CO$_2$–He complex with respect to a frame with its \( z \) axis along the vector \( \mathbf{R} \), which points from the center of mass of CO$_2$ to the He nucleus and the CO$_2$–He complex lying in the \( zx \)-plane. The coordinates are the length of the vector \( \mathbf{R} \), the angle \( \theta \) between the CO$_2$ axis and the vector \( \mathbf{R} \), and the normal coordinate \( Q \) (\( Q_1 \) or \( Q_3 \)) along which CO$_2$ is being deformed with respect to its linear equilibrium geometry with equal C–O bond lengths of 1.162 Å. The normal coordinate \( Q = c_1 \Delta z_1 + c_2 \Delta z_2 + c_3 \Delta z_3 \) is a linear combination of the displacements \( \Delta z_i \) of the atoms \( i = 1, 2, 3 \) along the CO$_2$ axis [the \( z \) axis in the monomer frame (MF)] with respect to their equilibrium positions \( z_0 \). The indices \( i = 1 \) and 3 label the O atoms, and \( i = 2 \) refers to the C atom. The coefficients of the symmetric stretch mode \( Q_1 \) obey the relations \( c_1 = -c_3 \) and \( c_2 = 0 \), while for the asymmetric stretch mode \( Q_3 \), we have \( c_1 = c_3 \) and the sign of \( c_2 \) is opposite to that of \( c_1 \) and \( c_3 \). They are obtained by calculating the normalized eigenvectors of the CO$_2$ monomer Hamiltonian in the harmonic-oscillator rigid-rotor approximation in mass-weighted coordinates and transforming them to Cartesian coordinates.

The 3D Hamiltonian of the vibrotor-atom system CO$_2$–He over the monomer normal coordinate \( Q \) is given, in the BF frame, by

\[
H = -\frac{\hbar^2}{2 \mu} \frac{\partial^2}{\partial R^2} + \hat{H}_{\text{CO}_2}(Q) + \frac{j^2 + \frac{1}{2} - 2j^2}{2 \mu R^2} + V(Q, R, \theta),
\]

where \( \mu = m_{\text{CO}_2} m_{\text{He}} / (m_{\text{CO}_2} + m_{\text{He}}) \) is the reduced mass of the complex, \( j \) is the CO$_2$ monomer rotational angular momentum operator, \( \hat{J} \) is the total angular momentum operator of the complex, and \( \hat{J}^2 \) represents the end-over-end angular momentum operator \( L^2 \) in the BF frame. The CO$_2$ monomer Hamiltonian is

\[
\hat{H}_{\text{CO}_2}(Q) = -\frac{\hbar^2}{2 \mu_{\text{CO}_2}} \frac{\partial^2}{\partial Q^2} + \frac{j^2}{2I(Q)} + V_{\text{CO}_2}(Q),
\]

where \( I(Q) = \sum m_i (z_i^2 + \Delta z_i)^2 \) is the instantaneous moment of inertia and \( V_{\text{CO}_2}(Q) \) is the 1D potential of isolated CO$_2$ for deformation along the normal coordinate \( Q \). The effective mass is \( \mu_{\text{CO}_2}(Q) = c_1^2 m_0 + c_2^2 m_c + c_3^2 m_o \). The eigenfunctions of the CO$_2$ monomer Hamiltonian are

\[
|v \Omega \rangle = \chi_v(Q) Y_{\Omega \ell}(\theta, \phi),
\]

and the corresponding eigenvalues are \( \epsilon_v \). Note that the vibrational functions \( \chi_v(Q) \) are \( f \)-dependent and the rotational functions \( Y_{\Omega \ell}(\theta, \phi) \) are spherical harmonics. The latter are expressed with respect to the BF frame, where the angle \( \theta \) is the same as defined above and the angle \( \phi \) coincides with the third Euler angle for the overall rotation of the complex. The quantum number \( \Omega \) is the projection of the CO$_2$ angular momentum \( j \) and of the total angular momentum \( \hat{J} \) onto the BF \( z \) axis along the vector \( \mathbf{R} \).

The channel basis in coupled-channel (CC) scattering calculations for rovibrationally inelastic CO$_2$–He collisions is, in BF coordinates,

\[
|v \Omega; J M \rangle = \chi_v(Q) Y_{\Omega \ell}(\theta, \phi) D_{\ell M}^J(\alpha, \beta, \phi)^* \sqrt{\frac{2J+1}{4\pi}}.
\]
The angles \((\beta, \alpha)\) are the polar angles of the vector \(R\) with respect to a space-fixed frame (SF), and the angles \((\alpha, \beta, \phi)\) in the Wigner D-functions describe the orientation of the BF frame relative to the SF frame. The angle \(\phi\) has been moved from the spherical harmonics in Eq. (3) to the overall rotation functions, which is mathematically equivalent. The so-called helicity quantum number \(\Omega\) is an approximate quantum number; basis functions with different \(\Omega\) are mixed by the Coriolis coupling operator \(\hat{J}\cdot\hat{J}\) in Eq. (1). When the 3D potential is expanded in Legendre polynomials \(P_l(\cos \theta)\) of order \(l\),

\[
V(Q, R, \theta) = \sum_{l} C_l(Q, R) P_l(\cos \theta),
\]

its matrix elements over the BF basis are

\[
V_{v'j'\Omega';MJ}(R) = \delta_{\Omega'\Omega} \delta_{l'l} \sum_{l} (-1)^{l'} [(2l' + 1)(2j' + 1)]^{1/2} \times \langle j' \lambda \lambda j \rangle \times \langle j' \lambda \lambda j \rangle \times \langle v'j'(Q) C_l(Q, R) | v(\bar{Q}) \rangle.
\]

The equivalent SF basis is given by

\[
|v\bar{J}\bar{L};JM\rangle = \sum_{\bar{m}M_\bar{l}} (jm_lLM_l|JM\rangle Y_{jm_l}(\theta^S, \phi^S) \times Y_{LM_l}(\alpha, \beta),
\]

where \((jm_lLM_l|JM\rangle)\) is a Clebsch–Gordan coefficient and \((\theta^S, \phi^S)\) are the polar angles of the CO\(_2\) axis with respect to the SF frame. The BF and SF bases are related by the unitary transformation

\[
|v\bar{J}\bar{L};JM\rangle = \sum_{\bar{J}} |v\bar{J}\bar{L};JM\rangle U_{\bar{J}J}^{\bar{L}L},
\]

with matrix elements

\[
U_{\bar{J}J}^{\bar{L}L} = \langle \bar{J}\bar{L}\bar{\Omega}|J\Omega \rangle \sqrt{\frac{2L + 1}{2J + 1}}.
\]

Equation (6) shows the advantages of the BF basis: the potential \(V(Q, R, \theta)\) does not mix functions with different \(\Omega\) and the expressions for its remaining matrix elements is simpler than in the SF basis,\(^5\) which makes the calculations more efficient.

The overall angular momentum quantum numbers \(J\) and \(M_J\) are constants of the motion, and the overall parity \(P\) under inversion of the system is also a conserved quantity. The BF basis in Eq. (4) is not invariant under inversion; a parity adapted basis is

\[
|v\bar{J}\bar{L};PJ;JM\rangle = \left[|v\bar{J}\bar{L};PJ;JM\rangle + P(-1)^{\bar{L}+\bar{J}} \times |v\bar{J} - \bar{L};PJ;JM\rangle \right] / \sqrt{2(1 + \delta_{\bar{J}0})},
\]

where \(\bar{\Omega} \geq 0\) and \(P = \pm 1\) is the overall parity. The SF basis in Eq. (7) is adapted to inversion with parity \(P = (-1)^{v'j'+j}\).

Another valid symmetry operation is the interchange \(P_{12}\) of the O atoms in CO\(_2\). This operator affects only the monomer wave functions in the bases of Eqs. (4) and (7). For the symmetric and asymmetric stretch modes that we consider here, we find

\[
\hat{P}_{12} |v\bar{J}\bar{L}\rangle = (-1)^v |v\bar{J}\bar{L}\rangle \quad \text{for} \quad v = v_1,
\]

\[
\hat{P}_{12} |v\bar{J}\bar{L}\rangle = (-1)^{v_2} |v\bar{J}\bar{L}\rangle \quad \text{for} \quad v = v_2.
\]

Since \(^{16}\)O nuclei, which are most abundant, are bosons with spin zero, the wave functions must be symmetric under \(\hat{P}_{12}\). This implies that for the symmetric stretch mode \(v_1\), only functions with even \(j\) are allowed, while for the asymmetric stretch mode \(v_2\), only functions with \(v_1\) and \(j\) both even or both odd are allowed.

The scattering wave functions in CC calculations are written in terms of the BF channel basis as

\[
\psi_{v'J'\Omega';JM}(R) = \frac{1}{\sqrt{4}} \sum_{vJ\Omega} |v\bar{J}\bar{L};PJ;JM\rangle \psi_{v\bar{J}\bar{L}}^{JM}(R).
\]

When these functions are substituted into the time-independent Schrödinger equation, it follows that the radial wave functions \(\psi_{v\bar{J}\bar{L}}^{JM}(R)\) must obey a set of second order differential equations, the CC equations. The procedure to solve these equations and match the solutions at large \(R\) to the appropriate asymptotic functions to obtain the scattering matrix \(S\) is a standard one.\(^6\) The asymptotic functions are defined in the SF frame and depend on the quantum number \(L\). Hence, in order to apply this procedure, we must transform our BF solutions at large \(R\) to the equivalent SF functions with the aid of Eq. (8). This procedure is followed for different values of \(J\) and both parities \(P = \pm 1\). From the \(S\)-matrices thus obtained, one computes the integral scattering cross sections

\[
\sigma_{v'\bar{J}'\bar{L}'\rightarrow v\bar{J}\bar{L};JPM}(E) = \frac{\pi}{(2J + 1)k_{\bar{E}}^2} \sum_{v'j'} \sum_{\bar{L}'j'} \sum_{J'P} \left| \delta_{v'j'j}\delta_{\bar{L}'L} - \delta_{v'j'j}\delta_{\bar{L}'L} \right|^2,
\]

where \(E\) is the total energy, \(k_{\bar{E}}^2 = 2 \mu (E - \epsilon_{v'j'})\), and \(\epsilon_{v'j'}\) is the energy of the initial state \(v,j\). The maximum value of \(J\) is chosen such that the cross sections are converged. Only the open channels, i.e., the final states with energies \(\epsilon_{v'j'}\) less than the total energy \(E\) have non-zero cross sections. Finally, from the cross sections calculated for a sufficient range of collision energies \(E\), one obtains the state-to-state rate coefficients at temperature \(T\),

\[
\kappa_{v'\bar{J}'\bar{L}'\rightarrow v\bar{J}\bar{L};JPM}(T) = \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \int_0^\infty \sigma_{v'\bar{J}'\bar{L}'\rightarrow v\bar{J}\bar{L};JPM}(E) \left( \frac{E}{k_B T} \right)^{3/2} \exp \left( \frac{-E}{k_B T} \right) d \left( \frac{E}{k_B T} \right),
\]

where \(k_B\) is the Boltzmann constant. The vibrational quenching rate for a transition from initial state \((v,j)\) to a final vibrational state \(v'\) is defined as the sum over all final rotational states \(j'\) in

\[
\kappa_{v'\bar{J}'\bar{L}'\rightarrow v\bar{J}\bar{L};JPM}(T) = \sum_{J'P} \kappa_{v'\bar{J}'\bar{L}'\rightarrow v\bar{J}\bar{L};JPM}(T).
\]
\[ k_{v'\rightarrow v}(T) = \frac{\sum(2j+1) \exp(-\epsilon_{v'j}/k_BT)k_{v'\rightarrow v}(T)}{\sum(2j+1) \exp(-\epsilon_{vj}/k_BT)}. \]  

(B. Multi-channel distorted-wave Born approximation)

The coupling matrix elements \( \langle v' \mid j' \rangle |C_i(Q,R)\rangle |vj(Q)\rangle \) in Eq. (6) for rovibrational transitions with \( v' \) different from \( v \) are much smaller than those for pure rotational transitions with \( v' = v \). This is because the CO\(_2\) monomer vibrational wave functions \( \chi_v(Q) \) for different vibrational quantum numbers \( v \) are orthogonal so that the integration over \( Q \) only gives a non-zero result for \( v' = v \) because the Legendre coefficients \( C_i(Q,R) \) of the 3D potential \( V(Q,R,\theta) \) are \( Q \)-dependent. Since this dependence is weak, the result is very small. Vibrational wave functions \( \chi_v(Q) \) with the same \( v \) and different \( j \) have a large overlap and the integral over \( Q \) is much larger than for \( v' \neq v \), also when \( j' \neq j \).

Because of this large difference in magnitude of the coupling matrix elements, we may partition the potential matrix in Eq. (6) as \( V = V_0 + \Delta V \), where \( V_0 \) contains the blocks of \( j',j \) elements diagonal in \( v, i.e., with v' = v \), and \( \Delta V \) contains the blocks of \( j',j \) elements for \( v' \neq v \). The elements of \( \Delta V \) are much smaller than those of \( V_0 \), so we may treat them as a perturbation of the scattering wave functions calculated with only \( V_0 \) included in the Hamiltonian. In scattering theory, this implies that one may obtain the cross sections for pure rotational transitions within the same \( v \) manifolds from separate CC calculations for each \( v \), while computing the cross sections for rovibrational transitions between different \( v \) manifolds with the use of a multi-channel distorted-wave Born approximation (MC-DWBA). The theory for the DWBA and MC-DWBA is explained in the textbook by Messiah,\(^{17}\) but the exact expressions that we use cannot be found there. The MC-DWBA expression for the S-matrix is given without derivation in Ref. 18 for collinear scattering. Since the exact expressions depend on the normalization and on the phase convention of the wave function and they are subtly different for \( S \)- and \( K \)-matrix boundary conditions, we present a derivation that illuminates the relation between the boundary conditions for the wave function and the MC-DWBA expressions in the Appendix. The SF scattering wave functions obtained by matching the solutions of the coupled-channels equations to \( S \)-matrix boundary conditions may be written as

\[ \psi^{(s)}_{vjK}M_l = \frac{1}{R} \sum_{l'j'} |v'j'LM_l\rangle \psi^{(+)}_{vjLM_l}(R). \]  

The quantum numbers in the superscripts \((\pm)vjLM_l\) label the asymptotic solutions, with \((+)\) referring to incoming waves and \((-)\) referring to outgoing waves. They are obtained from separate CC calculations for each \( v \). As derived in the Appendix, the \( S \)-matrix elements for transitions between different \( v \) manifolds, using flux-normalized scattering wave functions, are given in the MC-DWBA by the first-order perturbation formula\(^{17-19}\)

\[ S^{(l)}_{v'j'LM_l,jLM} = -\frac{i}{\hbar} \langle \psi^{(-)}_{v'j'LM_l}|\Delta V|\psi^{(+)}_{vjLM_l}\rangle. \]  

They do not depend on \( M_l \), so this quantum number may be omitted. The matrix elements in Eq. (6) over the basis \( |vjLM_l\rangle \) with the operator \( \Delta V \) belong to the perturbation matrix \( \Delta V \); they only differ from zero for \( v' \neq v \). The unperturbed matrix \( S^{(0)} \) is zero in this case.

The expression in Eq. (18) contains an integral over the radial wave functions \( \psi_{vjK}(R) \) over the full range of \( R \) values. Our scattering program, which uses the renormalized Numerov propagator,\(^{20,21}\) does not compute the scattering wave functions but propagates matrices \( Q_i \) over a radial grid with points \( R_i \) with \( i = 1, \ldots, n \). We use the BF channel basis defined in Eq. (4) and the corresponding radial wave functions \( \psi_{vjK}(R) \), and the \( Q \)-matrices are defined by

\[ \psi(R_i-1) = Q_i \psi(R_i), \]  

where the column vectors \( \psi(R_i) \) contain the radial functions \( \psi_{vjK}(R) \) of all channels \( |v\rangle \) at grid point \( R_i \). At the end of the propagation, the final matrices \( Q_{n-1} \) and \( Q_n \) are transformed into their SF equivalents

\[ Q^\text{SF}_i = U^\dagger Q_i U, \]  

with the matrix \( U \) from Eq. (9) and used in the matching procedure to obtain the \( S \)-matrix. In principle, we could store all matrices \( Q_i \) obtained during the propagation and use these to construct the full radial wave functions \( \psi_{vjK}(R) \) for \( i = 1, \ldots, n \). Instead, we use a much more efficient algorithm developed in our group. In this algorithm, derived and described in detail in Ref. 22, the matrices \( Q^{(v)} \) for different \( v \) and \( v' \) are propagated separately, but simultaneously. The coupling matrix \( \Delta V(R) \) with the matrix elements in Eq. (6) over the BF channel functions with \( v' \) different from \( v \) enters a matrix \( B_i \), which is propagated simultaneously with the matrices \( Q^{(v)} \) and \( Q^{(v')} \), with the formula

\[ B_i = Q^{(v')}\dagger B_{i-1}Q^{(v)} + \delta_k \Delta V(R_i), \]  

where \( \delta_k \) is the step size in the propagation. At the end of the propagation, the matrices \( Q^{(v)} \) and \( Q^{(v')} \) are transformed from the BF to the SF basis with the aid of Eq. (20) and used in the asymptotic matching procedure to obtain the \( S \)-matrices \( S^{(v)} \) and \( S^{(v')} \) and the corresponding asymptotic wave functions \( \psi^{(+)}_{vjLM_l} \) and \( \psi^{(-)}_{v'j'LM_l} \). Finally, the \( v'v \) coupling \( S \)-matrix is calculated from these asymptotic wave functions and the propagated coupling matrix \( B_i \),

\[ S^{(v'v)} = -\frac{i}{\hbar} \langle \psi^{(-)}_{v'j'LM_l}|\Delta V|\psi^{(+)}_{vjLM_l}\rangle, \]  

after transformation of \( B_i \) from the BF to the SF basis. The matrix \( S^{(v'v)} \) is combined with the matrices \( S^{(v)} \) and \( S^{(v')} \) to obtain the full \( S \)-matrix over all rovibrational channels and used in Eqs. (13) and (14) to obtain state-to-state cross sections and rate coefficients for all rovibrationally inelastic transitions.

The \( S \)-matrix is a complex-valued unitary symmetric matrix, and we actually use the real-valued symmetric \( K \)-matrix as an intermediate. We first match the solutions of the coupled-channels equations for \( v \) and \( v' \) to \( K \)-matrix boundary conditions, which yields the matrices \( K^{(v)} \) and \( K^{(v')} \) and the corresponding real-valued scattering wave functions. These wave functions are then substituted into Eq. (A37) of the Appendix, which yields the coupling matrix \( K^{(v'v)} \).
From the full K-matrix with diagonal blocks $K^{(v)}$ and $K^{(v')}$ and off-diagonal blocks $K^{(v'v)}$ and $K^{(v'v')}$, we obtain a unitary S-matrix through Eq. (A38).

Basically, the same MC-DWBA formalism and algorithm were successfully applied to compute rotational state-to-state cross sections and rate coefficients for para–ortho H$_2$ conversion in O$_2$–H$_2$ collisions. In that case, the matrix $V$ contained the matrix elements over the anisotropic O$_2$–H$_2$ potential and the two simultaneous CC calculations yielded the cross sections and rates for rotational transitions within the para-H$_2$ species with even $j$ and the ortho-H$_2$ species with odd $j$. The MC-DWBA method applied with the much smaller “perturbation” matrix $\Delta V$ containing matrix elements over the relevant hyperfine terms that couple para-H$_2$ with ortho-H$_2$ yielded the cross sections and rate coefficients for para–ortho H$_2$ conversion.

C. Rotational sudden approximation

Since we will also show some results calculated with the vibrational close-coupling rotational infinite-order sudden (VCC-IOS) approximation used by Clary et al. we briefly outline the basics of this approach. The IOS approximation is based on the assumption that the collision time is much shorter than the time it takes the molecule to rotate so that one may carry out scattering calculations in which the orientation of the molecule stays fixed. The channel basis contains only the vibrational wave functions of the monomer, and its rotational states are omitted. The monomer rotational kinetic energy is also omitted from the Hamiltonian, and in the centrifugal term, it is assumed that the end-over-end angular momentum $L$ is equal to the total angular momentum $J$. Scattering calculations are carried out for a representative number of fixed molecular angles $0 \leq \theta \leq \pi$ with the anisotropic intermolecular potential taken at these fixed angles, which yields the S-matrices $S_{\theta,J}^{(v)}(\theta,E)$. The integral cross sections at collision energy $E$ can be computed from

$$\sigma_{v'v}(E) = \frac{\pi}{2k^2} \int_0^\pi d\theta \sin \theta \sum_{J=0}^{\infty} (2L+1) \left| \delta_{v'v} - S_{\theta,J}^{(v)}(\theta,E) \right|^2, \quad (23)$$

where $k^2 = 2 \mu (E - \epsilon_v)$ and $\epsilon_v$ is the energy of vibrational state $v$. In our calculations, we take angles $\theta_i$ corresponding to a Gauss–Legendre quadrature grid and we compute the integral over $\theta$ with Gauss–Legendre quadrature. It turns out that ten angles are sufficient to probe the anisotropy of the potential. The vibrational–coupled-channel equations are solved with the renormalized Numerov propagator, as in our full rovibrational CC calculations, and the asymptotic matching procedure to obtain the S-matrix is also the same.

By projection of the S-matrices for different angles $\theta$ onto the initial and final rotational states $j$ and $j'$ of the molecule, it would also be possible, in principle, to obtain the cross sections for specific rovibrational transitions. However, Clary et al. calculated only the cross sections for vibrational transitions, irrespective of the initial and final rotational states. Hence, their rate coefficients should be compared with our values from Eq. (16). However, the VCC-IOS results only depend on the temperature through the energy dependence of the cross sections $\sigma_{v'v}(E)$, whereas our vibrational rate coefficients from rovibrational state-to-state calculations and Eq. (16) also depend on the temperature through the occupations of the initial rotational states.

III. COMPUTATIONAL DETAILS

A. Vibrational wave functions of CO$_2$

We started the calculations with the computation of the equilibrium geometry and force constant matrix of free CO$_2$ using the MOLPRO 2015 program. We used the coupled-cluster method with single and double excitations and perturbative triplets CCSD(T) and the augmented quadruple-zeta correlation-consistent polarized (aug-cc-pVQZ) basis of Dunning. Harmonic-oscillator calculations with this force constant matrix yielded normal coordinates $Q_i$ with atomic displacement coefficients $c_1 = -c_3 = 0.17678\, a_0$ and $c_2 = 0$ for the symmetric stretch mode and $Q_j$ with coefficients $c_1 = c_3 = 0.09235\, a_0$ and $c_2 = -0.24604\, a_0$ for the asymmetric stretch mode. The normal mode eigenvectors are normalized in mass-weighted coordinates, so the effective mass is 1 u. The calculated harmonic frequencies and force constants are 1346.1 cm$^{-1}$ and 0.06 8 55 $E_{ij}a_0^{-2}$ for the $v_1$ mode and 2408.7 cm$^{-1}$ and 0.2196 $E_{ij}a_0^{-2}$ for the $v_3$ mode. Then, we obtained one-dimensional (1D) potentials $V_{CO_2}(Q)$ for the symmetric and asymmetric stretch modes by calculating the energies for deformation of the CO$_2$ molecule along the normal coordinates $Q_1$ and $Q_3$, respectively, also using the CCSD(T) method and the same basis. These potentials were calculated on equidistant grids with 29 points ranging from $Q$ to $Q$ to also probe the anharmonicity and then used to compute the eigenfunctions of the monomer Hamiltonian in Eq. (2) with the sinc–discrete variable representation (DVR) method. Repeating this for different values of the rotational quantum number $j$ yields the monomer vibrational wave functions $\chi_{j,v}(Q)$ for $Q = Q$ and $Q = Q$.

B. Three-dimensional CO$_2$–He potential

The 3D potential surfaces $V(Q,R,\theta)$ for $Q = Q_1$ and $Q = Q_3$ were calculated with the CCSD(T) method and the aug-cc-pVTZ basis extended with a set of 3s3p2d1f midbond functions with geometry-dependent exponents. These midbond functions were placed on the intersection of the vector R with an ellipse defined around CO$_2$. This ellipse is chosen such that they are located at the midpoint of $R$ in the T-shaped configuration and on the midpoint of the vector connecting He and the nearest O atom in the linear configuration. The geometry-dependent exponents and elliptical locus prevent overcompleteness of the midbond and atomic basis in the short range. Interaction energies were obtained in the supermolecule approximation as $V_{CO_2-He} = E_{CO_2-He} - E_{CO_2} - E_{He}$ with the same one-electron basis for the complex and the monomers to correct for the basis set superposition error (BSSE). Since the intermolecular potential nearly linearly depends on the molecular deformation $Q$, we only chose three points in $Q$: at the equilibrium geometry $Q = 0$ and with positive and negative displacements $Q_1 = \pm 0.73$ and $Q_3 = \pm 0.5232$ for the symmetric and asymmetric stretch modes, respectively. These displacements correspond to the classical turning points of the $v = 2$ vibrational energy level in the monomer’s 1D potentials $V_{CO_2}(Q)$ for $Q = Q_1$ and $Q = Q_3$. We chose eight Gauss–Legendre quadrature points in the range from 0 to $\pi/2$ for the angle $\theta$. The radial grid consisted of 48 points $R$ in the range from 3
to $25a_0$. The total number of symmetry-unique geometry points was 1152. For all geometries, the $T_1 \propto 1/\sqrt{N}$ diagnostic, where $N$ is the number of correlated electrons, was less than 0.018, which indicates that the CCSD(T) method is reliable.

An analytical representation of the 3D potential was obtained from the *ab initio* points as follows. First, we expanded the angular dependence of the potential for fixed values $Q_i$ and $R_j$ in Legendre polynomials, as in Eq. (5). The expansion coefficients $C_i(Q_i, R_j)$ are easily obtained by Legendre quadrature

$$C_i(Q_i, R_j) = \frac{2l + 1}{2} \sum_k w_k V(Q_i, R_j, \theta_k) P_l(\cos \theta_k),$$

(24)

where $w_k$ are the weights corresponding to the Legendre quadrature points $\theta_k$. With eight points in the region from 0° to 90° and use of the symmetry, we could obtain the expansion coefficients for $\lambda = 0$ to 15. Then, these coefficients were written as

$$C_i(Q_i, R_j) = \sum_{p=0}^{2} \gamma_{pi}(R_j) Q^p,$$

(25)

with coefficients $\gamma_{pi}(R_j)$ fitted to the potential calculated at the three-point grid of $Q_i$ values. Finally, the $R$ dependence of these coefficients was represented by the reproducing kernel Hilbert space (RKHS) method with the smoothness parameter $m = 2$. The parameter $m$ in this method ensures that the potential decays with $1/R^{m-1}$ for $R$ values beyond the largest grid point $R_1$. We chose $m = 5$ for the coefficients with $\lambda = 0, 1, 2$, which decay as $1/R^3$ and $m = \lambda + 3$ for higher values of $\lambda$.

Some extremely high and steep peaks in the repulsive part of the potential occur at specific geometries with small values of $R$. They are not physically important because the system cannot reach these geometries even at the highest collision energies, but they would spoil the convergence of the Legendre expansion in Eq. (5). In order to avoid this, we damped the potential for values larger than $V_0 = 0.1E_0$ with a smooth damping function

$$V_{\text{damped}}(Q, R, \theta) = V_0 + \tanh(\beta [V(Q, R, \theta) - V_0])/\beta,$$

(26)

where $\beta = 1/V_0$ and $2V_0$ is the maximum value of the damped potential. The value of $R$ where this damping was applied depends on the angle $\theta$. For the T-shaped structure with $\theta = 90°$, no damping was needed, and for the linear structure with $\theta = 0°$ or 180°, the damping was applied for $R \leq 4.5a_0$.

With a complete analytic representation of the 3D CO$_2$–He potential $V(Q, R, \theta)$ available, we can look at some features of this potential. For CO$_2$, in its equilibrium geometry, it has a global minimum with well depth $D_e = 47.43$ cm$^{-1}$ at a T-shaped structure ($\theta = 90°$) for $R_e = 5.81$ a$_0$. It has two equivalent local minima with a depth of 26.60 cm$^{-1}$ for linear geometries with $R = 8.06a_0$. We may compare this with some *ab initio* CO$_2$–He potentials in the literature. Three-dimensional CO$_2$–He potentials depending on the asymmetric stretch coordinate were also calculated by Ran and Xie and by Li and Le Roy. The global minimum at the T-shaped structure in these potentials has a depth of 49.39 and 49.57 cm$^{-1}$, respectively, with equilibrium distances $R_e$ of 5.79 and 5.78 a$_0$. They also have local minima at the linear structure with depths 26.70 and 26.69 cm$^{-1}$ at $R = 8.06$ a$_0$. The 2D potential calculated earlier by Korona et al. has a global minimum with $D_e = 50.38$ cm$^{-1}$ and $R_e = 5.81$ a$_0$ and two local minima with a depth of 28.94 cm$^{-1}$ at $R = 8.03$ a$_0$.

We may also look at the 2D potentials obtained by averaging our 3D CO$_2$–He potential over the ground state vibrational wave functions of CO$_2$ for the $v_1$ and $v_3$ modes. The corresponding $D_e$ values are 47.52 and 47.33 cm$^{-1}$ for the $v_1$ and $v_3$ modes, respectively, with $R_e = 5.80$ and 5.81 a$_0$.

The potential is strongly anisotropic, which is illustrated in Fig. 1, which shows the different coefficients in the Legendre expansion of Eq. (24) as functions of $R$ at $Q = 0$. At the symmetric equilibrium structure, only terms with even $\lambda$ contribute to the expansion.

In the short range, the leading anisotropic expansion coefficient $C_2(0, R)$ is even larger than the isotropic coefficient $C_0(0, R)$, and $C_4(0, R)$ is also substantial. In the long range, the expansion converges faster. When CO$_2$ is deformed along the asymmetric stretch mode $Q_3$, terms with odd $\lambda$ also contribute. Figure 2 shows the 3D intermolecular potential at the equilibrium geometry of CO$_2$ and the change in the potential when CO$_2$ is deformed along the asymmetric stretch mode with $Q_3 = 0.5$. It is plotted in the Cartesian coordinates $z = R \cos \theta$ and $x = R \sin \theta$.

C. Scattering calculations

Scattering calculations are performed with the CC method and the MC-DWBA approach, as described in Sec. II. Additionally, we made VCC-IOS calculations for comparison with the older results of Clary et al. We used our own programs, based on the renormalized Numerov propagator, with a radial grid ranging from 3 to 30 a$_0$ in 502 steps. We included the vibrational states of CO$_2$ with quantum numbers $v = 0$ and 1, for the symmetric and asymmetric stretch modes. In test calculations, we added the $v = 2$ states to the basis, but since this changed the cross sections by less than 0.5%, we did not include these in the final calculations. Rotational
functions of CO$_2$ of up to $j = 70$ for the $v_1$ mode and $j = 100$ for the higher energy $v_2$ mode were included in the channel basis, both for $v = 0$ and 1. After various convergence tests, we made calculations for total angular momenta $j$ of up to 100, for both parities $P$.

Rovibrational state-to-state cross sections were calculated for collision energies of up to 3000 cm$^{-1}$, with steps of 0.1 cm$^{-1}$ in the resonance regime from 1 $\leq E \leq$ 20 cm$^{-1}$, steps of 1 cm$^{-1}$ for 20 $\leq E \leq$ 50 cm$^{-1}$, 2 cm$^{-1}$ for 50 $\leq E \leq$ 100 cm$^{-1}$, 50 cm$^{-1}$ for 100 $\leq E \leq$ 1000 cm$^{-1}$, and 200 cm$^{-1}$ for 1000 $\leq E \leq$ 3000 cm$^{-1}$. The corresponding rate coefficients were calculated for temperatures from 10 to 500 K by spline interpolating the cross sections over the energy grid and calculating the integral in Eq. (14) with the trapezoidal rule. Since the rotational states of CO$_2$ of up to $j = 50$ with energy 991 cm$^{-1}$ are populated at the highest temperature, we calculated the cross sections and rate coefficients for initial states up to this value of $j$.

IV. RESULTS AND DISCUSSION

A. Cross sections

First, we compare the cross sections for vibrational $v = 1 \rightarrow 0$ quenching calculated with the VCC-IOS method used by Clary et al.$^{10-13}$ with $v = 1 \rightarrow 0$ cross sections obtained with the CC method. The latter are calculated for specific initial and final rotational states $j$ and $j'$ of CO$_2$ but were summed over all final $j'$ states for the purpose of this comparison. The results for the symmetric ($v_1$) and asymmetric ($v_3$) stretch modes are shown in Fig. 3. Only even $j$ and $j'$ values are allowed for the $v_1$ mode, and we took the initial state with $v_1 = 1, j = 0$. Only odd $j$ values are allowed for the excited $v_3$ state with $v_3 = 1$, and we used an initial state with $j = 1$. However, it will be shown below that the sum of the state-to-state cross sections over all final $j'$ values hardly depends on the initial $j$ value so that averaging the summed CC cross sections over all initial $j$ would show very similar results. Actually, this averaging should be Boltzmann weighted over all initial $j$ states that are thermally populated, but this is not possible in the VCC-IOS method.

Figure 3 shows that the VCC-IOS method underestimates the $v = 1 \rightarrow 0$ quenching cross sections by about one order of magnitude for the $v_1$ mode and by about two orders of magnitude for the $v_3$ mode at higher collision energies. For low collision energies, the differences are even larger. The difference between the two modes seems to correlate with the magnitude of the quenching cross sections: in the $v_3$ mode, they are smaller by a few orders of magnitude than in the $v_1$ mode. The peaks in the cross sections at energies below 20 cm$^{-1}$ are due to scattering resonances. The VCC-IOS method does not capture the resonances from CC calculations, but they only play a role on the quenching rate coefficients at low temperatures.

We found two values for the same rate coefficient in Clary’s papers that we can compare with our value. In Table VI of Ref. 10, the rate coefficient for the symmetric stretch mode at $T = 300$ K is given as $0.69 \cdot 10^{-14}$ molecule$^{-1}$ cm$^3$ s$^{-1}$, and in Table 6 of Ref. 11, it is $0.15 \cdot 10^{-14}$ molecule$^{-1}$ cm$^3$ s$^{-1}$. Our value for the symmetric stretch mode at $T = 300$ K is $0.39 \cdot 10^{-14}$ molecule$^{-1}$ cm$^3$ s$^{-1}$. Clary’s values were calculated with two different approximate CO$_2$–He potentials, and ours were calculated with the potential given in the present paper, so the result clearly depends on the potential.

In Fig. 4, we show state-to-state $v = 1 \rightarrow 0$ quenching cross sections from CC calculations for selected initial $j$ and final $j'$ values. The cross sections for the $v_1$ mode are larger than those for the $v_3$ mode by several orders of magnitude. This is in agreement with the energy gap law: the vibrational frequencies are 1333 and 2349 cm$^{-1}$ for the $v_1$ mode and for the $v_3$ mode, respectively.

The trends in the $v = 1, j \rightarrow v' = 0, j'$ state-to-state quenching cross sections for different initial $j$ and final $j'$ values are determined by two effects. First, the energy gap law favors quenching for low initial $j$ values to rather high final $j'$ values. It is of interest in this respect that the $v = 1, j = 0$ state in the $v_1$ mode has nearly the same energy as the $j' = 58$ level in the $v' = 0$ vibrational ground state, while the $v = 1, j = 1$ state in the $v_3$ mode lies between the $j' = 76$ and 78 levels in the $v' = 0$ state. Hence, according to the energy gap law, transitions between these states should be favored. They correspond to very large $\Delta j = j' - j$ values, however, and although the CO$_2$–He potential is strongly anisotropic, it favors transitions with smaller $\Delta j$.

The state-to-state cross sections shown in Fig. 4 demonstrate that, indeed, both effects play a role.

The left-hand panels of Fig. 4 for the symmetric stretch mode show that for collision energies of about 40 cm$^{-1}$, the $v = 1, j = 0 \rightarrow v' = 0, j' = 0$ cross section is largest, but that transitions to larger
FIG. 3. Integral cross sections from VCC-IOS calculations, compared with cross sections from CC calculations summed over final rotational states.

FIG. 4. State-to-state integral cross sections from CC calculations.
$j'$ values become favored for collision energies above 700 cm$^{-1}$. The middle and lower panels of Fig. 4 show that this trend to favor transitions to higher final $j'$ values becomes stronger when the initial $v = 1$ state is also rotationally excited. The right-hand panels of Fig. 4 for the asymmetric stretch mode show similar effects, but the trend to favor transitions to higher final $j'$ values is stronger here because of the larger $v = 1 \rightarrow v' = 0$ energy gap. Another phenomenon that can be observed in Fig. 4 is that low energy resonances (the sharp peaks in the cross sections) occur especially for the $v = 1$ initial state with the lowest allowed $j$ value (shown in the upper panels) and become less prominent with increasing initial $j$ values.

An extreme case of the energy gap and $\Delta j$ dependence is illustrated by the $j' = 58$ curves shown in the left-hand panels of Fig. 4. The energy gap is nearly zero for the $v' = 0, j' = 58$ final state for the initial state with $v = 1, j = 0$, but $\Delta j$ is very large. One can see in Fig. 4 that the corresponding cross sections are extremely small at low collision energies, but they become comparable with the largest cross sections for other $j'$ states at the highest collision energy when $\Delta j$ is somewhat reduced by increasing the initial $j$ value.

Figure 5 demonstrates that state-to-state cross sections obtained from MC-DWBA calculations agree very well with the corresponding results from full CC calculations. This holds for all collision energies and for both the $\nu_1$ and $\nu_3$ modes, and it is striking that even the individual resonances in the CC cross sections are accurately reproduced by the MC-DWBA method. Another way of comparing MC-DWBA and CC results is by looking at the rotational product distributions from vibrationally inelastic $v = 1 \rightarrow v' = 0$ scattering. Figure 6 shows these $v' = 0, j'$ product distributions at three different collision energies for the $\nu_1$ and $\nu_3$ modes. Again, the agreement between MC-DWBA and full CC is found to be almost perfect.

The left-hand panel in Fig. 7 shows the $v = 1, j \rightarrow v' = 0, j'$ quenching cross sections for the $\nu_1$ mode, summed over all final $j'$ states accessible at the given energy. For collision energies above 50 cm$^{-1}$, they are practically the same for all initial $j$ values. At lower energies, they are more and more affected by resonances, which are sensitive to the initial $j$ value. Similar conclusions apply to the quenching cross sections summed over all final $j'$ states shown in the right-hand panel of Fig. 7 for the $\nu_3$ mode.

B. Rate coefficients

State-to-state quenching rate coefficients obtained from the corresponding cross sections with the use of Eq. (14) are shown in Fig. 8 for the $\nu_1$ and $\nu_3$ modes. The observation that the cross sections for the $\nu_1$ mode are much larger than for the $\nu_3$ mode translates into a similar ratio of the rate coefficients. The rate coefficients show minima at temperatures between 20 and 60 K, which are related to the minima in the cross sections for collision energies from about 30 to 60 cm$^{-1}$. The strong increase in the rate...
FIG. 6. Comparison of product distributions from CC and MC-DWBA calculations.

FIG. 7. $v = 1 \to 0$ quenching cross sections summed over all final $j'$ states for different initial $j$ values from CC calculations.
FIG. 8. State-to-state rate coefficients from CC calculations for different initial $j$ values.

FIG. 9. $v = 1 \rightarrow 0$ quenching rate coefficients from CC calculations for different initial $j$ states, summed over final $j'$ values.
coefficients with increasing temperature also follows from the strong increase in the cross sections at higher energies. This behavior is typical for vibrationally inelastic processes: at high energy, i.e., high relative velocity, the colliding partners penetrate the repulsive short range interaction region, where the intermolecular potential most strongly depends on the vibrational coordinates of the molecule, CO$_2$ in this case. The upper panels of Fig. 8 show that the rate coefficients from MC-DWBA calculations also agree very well with those from full CC calculations.

More or less the same $\Delta j$ and energy gap dependence discussed for the $v = 1, j \rightarrow v', j'$ state-to-state cross sections for different $j$ and $j'$ are followed by the rate coefficients. The conclusion that the quenching cross sections summed over final $j'$ states are nearly independent of the initial $j$ value also holds for the rate coefficients shown in Fig. 9. Differences for different initial $j$ values occurring at temperatures below 70 K are caused by the resonances in the cross sections at low collision energies, which are sensitive to the initial $j$.

The detailed resonance structures in the cross sections for individual $j$ values are smoothed out in the rate coefficients by the integration over the collision energy.

The quenching rate coefficients from CC calculations shown in Fig. 9 were also obtained by MC-DWBA calculations. We do not show the corresponding curves, however, because they practically coincide with the CC results for the $v_1$ mode at all temperatures and for the $v_2$ mode at temperatures of up to about $T = 300$ K. The very small deviation of the MC-DWBA rates from the CC rates for the $v_1$ mode at higher temperatures is caused by small differences between the MC-DWBA and CC cross sections for transitions to higher final $j'$ states at collision energies above 1800 cm$^{-1}$.

We did not calculate the total vibrational quenching rate coefficients by Boltzmann averaging over the thermally occupied initial $j$ states. State-to-state data as presented here are meant to be applied to CO$_2$–He collisions in non-LTE conditions (i.e., without local thermal equilibrium), so this would not be very meaningful. However, our results demonstrate that the vibrational transition rate coefficients summed over all accessible final $j'$ values are practically independent of the initial $j$ values, except for temperatures below 70 K. Rate coefficients obtained by Boltzmann averaging over thermally occupied initial $j$ states would therefore be nearly the same as the rate coefficients shown in Fig. 9 for specific initial $j$ states.

C. Computational aspects

Another point that may be discussed is how much faster are MC-DWBA calculations than full CC calculations. Our calculations show that this is by about a factor of 3. This can be rationalized as follows. The separate propagation of the $v = 1, j$ and $v' = 0, j'$ states in the MC-DWBA method involves matrices that are about half the size of the matrices occurring in the full CC propagation of all states. The time needed for the matrix manipulations during propagation approximately scales with the third power of the matrix size. This implies that the simultaneous, but separate propagation of the $v = 1, j$ and $v' = 0, j'$ states in MC-DWBA takes about one quarter of the time of the full CC propagation. The $v = 1, j \rightarrow v' = 0, j'$ coupling matrix must also be simultaneously propagated in MC-DWBA, which takes nearly the same time as the propagation of each of the $v = 1, j$ and $v' = 0, j'$ blocks. Altogether this explains why MC-DWBA is faster than full CC by about a factor of 3. The MC-DWBA method is also advantageous over full CC calculations because it requires nearly a factor of 2 less memory.

V. CONCLUSIONS

We propose an efficient computational method based on a multi-channel distorted-wave Born approximation (MC-DWBA) to calculate state-to-state cross sections and rate coefficients for rovibrational $v, j \rightarrow v', j'$ transitions in molecular collisions. After computing and fitting the state-of-the-art ab initio three-dimensional potential energy surfaces for CO$_2$–He with CO$_2$ distorted along the symmetric and asymmetric stretch ($v_1$ and $v_2$) coordinates, this method is applied to the astrophysically important case of CO$_2$–He collisions. The resulting cross sections and rate coefficients are compared with those from nearly exact coupled-channel (CC) calculations. The results, summed over rotational states, are also compared with those of the more approximate VCC-IOS method applied by Clary et al. The VCC-IOS method yields only the total vibrational $v \rightarrow v'$ transition cross sections and rate coefficients.

The cross sections and rate coefficients from VCC-IOS calculations are too much small in comparison with accurate CC results calculated on the same potentials, by 1–2 orders of magnitude for the symmetric stretch ($v_1$) mode and by two to three orders of magnitude for the asymmetric stretch ($v_2$) mode. The cross sections for the $v_1$ mode are larger by one to two orders of magnitude than those for the $v_2$ mode, so it seems that the quality of VCC-IOS ameliorates with the magnitude of the cross sections. If this is, generally, true, it would explain why the VCC-IOS method seems to work reasonably well for the bend $v_2$ mode of CO$_2$–He. MC-DWBA and CC calculations on this bend mode are in progress.

The MC-DWBA results agree very well with the CC results for CO$_2$–He collisions, for both the $v_1$ and $v_2$ modes. Even the complicated resonance structures in the cross sections from CC calculations at low collision energies are accurately reproduced in MC-DWBA calculations. Hence, we may conclude that the MC-DWBA method as presented and applied here is not only efficient but also accurate.

The MC-DWBA method outlined and illustrated in this paper for transitions between two vibrational states $v$ may be extended to processes in which multiple $v$ states are involved. The coupling matrix $V$ with the elements over rovibrational states $v, j$ and $v', j'$ given in Eq. (6) should then be partitioned into a matrix $V_0$ that includes all states with equal $v$ and $v'$ and a perturbation matrix $AV$ with the blocks that contain the states with different $v$ and $v'$. If it turns out that the couplings in certain blocks of $AV$ lead to smaller transition cross sections and rate coefficients, these blocks may be left out from $AV$ and treated in separate calculations with the $v$ and $v'$ states that are coupled by these blocks. For CO$_2$, for example, the states involved could be the bend fundamental with $v_2 = 1$ at 667 cm$^{-1}$, the symmetric stretch fundamental $v_1 = 1$ at 1333 cm$^{-1}$, and the vibrational ground state. If it turns out that vibrational quenching from the $v_1 = 1$ stretch state is strongly dominated by transitions to the $v_2 = 1$ bend state rather than to the vibrational ground state, the latter may be left out from the calculations.

We are currently calculating rovibrational state-to-state cross sections and rate coefficients for transitions from the $v_2 = 1$ bend state to the ground state, and we are considering the $v_1 = 1$ symmetric stretch state in Fermi resonance with the $v_2 = 2$ bend overtone.
SUPPLEMENTARY MATERIAL

See the supplementary material for the Fortran programs to calculate the two potential surfaces derived in this work.

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APPENDIX: DERIVATION OF THE MC-DWBA

1. Basic derivation

First, we consider a single particle moving along a Cartesian coordinate \(x\), with the boundary condition that the wave function is zero at \(x = 0\).

The Wronskian of functions \(f\) and \(g\), which may be real or complex, is defined by

\[
W(f, g) = f(x)g'(x) - f'(x)g(x). \tag{A1}
\]

The derivative of the Wronskian is

\[
\frac{\partial}{\partial x} W(f, g) = f(x)g''(x) - f''(x)g(x), \tag{A2}
\]

so

\[
\int_a^b [f(x)g''(x) - f''(x)g(x)] \, dx = W(f, g)_{a}^{b}. \tag{A3}
\]

The Hamiltonian of a particle with mass \(\mu\) moving in one dimension is

\[
\hat{H}_0 = \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + V(x). \tag{A4}
\]

Thus, with Eq. (A3), we have

\[
\int_a^b \left( f(x)\hat{H}_0 g - g\hat{H}_0 f \right) \, dx = -\frac{\hbar^2}{2\mu} W(f, g)_{a}^{b} \tag{A5}
\]

since in the integrand, the contribution of the potential \(V\) cancels. Note that the term on the right-hand side (rhs) of the equation is nonzero, in general. This means that if, e.g., the function \(g\) is an eigenfunction, the Hamiltonian will not “operate to the left” in the second term of the integrand and the two terms will not cancel, in general. In addition, note that there is no complex conjugation in this expression. Next, consider a perturbation \(\Delta V\),

\[
\hat{H} = \hat{H}_0 + \Delta V. \tag{A6}
\]

The wave function \(\Psi(x)\) at energy \(E\) satisfies

\[
(H - E)\Psi(x) = 0, \tag{A7}
\]

and for the zeroth-order solution \(\Psi_0(x)\), we have

\[
(H_0 - E)\Psi_0(x) = 0. \tag{A8}
\]

For the perturbation in the wave function

\[
\Delta \Psi = \Psi - \Psi_0, \tag{A9}
\]

we have, in first order,

\[
(E - \hat{H}_0)\Delta \Psi = \Delta V \Psi_0, \tag{A10}
\]

where we dropped the second order term \(\Delta V \Delta \Psi\). In order to compute matrix elements, we define the usual scalar product with complex conjugation in the bra

\[
\langle \Psi_1 | \Psi_2 \rangle = \int_0^{\infty} \Psi_1^*(x) \Psi_2(x) \, dx. \tag{A11}
\]

Next, we project Eq. (A10) with \(\Psi_0^*\) and use Eq. (A5) to rewrite the left-hand side as

\[
\langle \Psi_0^* | \Delta V | \Psi_0 \rangle = \left[ \int_0^{\infty} \Psi_0^*(x) \Delta V \Psi_0(x) \, dx \right]_{(0)}^{(\infty)} = \frac{\hbar^2}{2\mu} W(\Psi_0, \Delta \Psi)_{(0)}^{(\infty)}. \tag{A12}
\]

Note that by using \(\Psi_0^*\) in the bra, we have \(\Psi_0(x)\) in the integrand and Eq. (A5) applies. Substituting Eq. (A10) into the remaining lhs of Eq. (A12) gives

\[
\langle \Psi_0^* | \Delta V | \Psi_0 \rangle = \frac{\hbar^2}{2\mu} W(\Psi_0, \Delta \Psi)_{(0)}^{(\infty)}. \tag{A13}
\]

We only consider perturbations \(\Delta V(x)\), which are negligible beyond some value \(x = x_{\text{max}}\), so on the rhs, the Wronskian can be evaluated for any \(x \geq x_{\text{max}}\). Furthermore, the functions \(\Psi_0\) and \(\Psi\), and hence also \(\Delta \Psi\), satisfy the boundary condition at \(x = 0\), so the Wronskian at \(x = 0\) will be zero. The outgoing wave \(S\)-matrix boundary conditions, for large \(x\), are

\[
\Psi^{(+)}(x) \equiv u(x) + v(x)S, \tag{A14}
\]

with

\[
u(x) = -Ne^{-ikx}, \tag{A15}
\]

where \(N\) is the normalization of the wave functions. For the zeroth-order solution, we have

\[
\Psi_0^{(+)}(x) \equiv u(x) + v(x)S_0. \tag{A16}
\]

Subtracting Eq. (A16) from Eq. (A14) gives

\[
\Delta \Psi(x) \equiv v(x)(S - S_0), \tag{A17}
\]

and so for large \(x (x \rightarrow \infty)\), we have

\[
W(\Psi_0^{(+)}(x), \Delta \Psi) = W[u + vS_0, v(S - S_0)] = W[u, v](S - S_0), \tag{A18}
\]

where we used that \(S\) and \(S_0\) do not depend on \(x\), and so they can be taken out of the Wronskian and \(W[u, v] = 0\). Combining Eqs. (A18) and (A13), we get the DWBA expression for the \(S\)-matrix,

\[
S = S_0 + \frac{2\mu}{\hbar^2 W[u, v]} W(\Psi_0^{(+)}, \Delta \Psi) \Psi_0^{(+)}), \tag{A19}
\]

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where the function with incoming wave boundary conditions, $\Psi^{(-)}$, is the complex conjugate of the function with outgoing wave boundary conditions. For flux-normalized wave functions, we have

$$N = \sqrt{\frac{\mu}{\hbar k}}$$  \hspace{1cm} (A20)

so $W(u, v) = -2ikN^2 = -2i\mu/\hbar$ and

$$S = S_0 + \frac{i}{\hbar} \langle \Psi^{(-)} | \Delta V | \Psi^{(+)} \rangle.$$  \hspace{1cm} (A21)

For scattering wave functions $\Psi_k$ with $K$-matrix boundary conditions, the functions $u$ and $v$ above are replaced by $f(x) = N \sin(kx)$ and $g(x) = N \cos(kx)$, where we keep the same normalization constant $N$. With $W(N \sin kx, N \cos kx) = -kN^2 = \mu/\hbar$, we find the DWBA for the $K$-matrix,

$$K = K_0 - \frac{2}{\hbar} \langle \Psi^{(K)} | \Delta V | \Psi^{(K)} \rangle.$$  \hspace{1cm} (A22)

2. The three-dimensional multichannel

In the multichannel case, the wave function is expanded as

$$\Psi(R, q) = \sum_n \phi_n(q) \frac{\psi_n(R)}{R},$$  \hspace{1cm} (A23)

where $R$ is the Jacobi scattering coordinate and all other coordinates are denoted as $q$. The volume element for integration can be written as $R^2 dR \rho(q) dq$, where the factor $\rho(q)$ depends on the choice of coordinates $q$. The channel functions are orthonormal,

$$\langle \phi_n | \phi_m \rangle = \int \phi_n^*(q) \phi_m(q) \rho(q) dq = \delta_{nm}.$$  \hspace{1cm} (A24)

The set of channel quantum numbers $n$ includes the partial wave quantum number $L$. The Hamiltonian is written as the sum of the radial kinetic energy operator plus the remainder,

$$\hat{H}_0 = -\frac{\hbar^2}{2k} \frac{\partial^2}{\partial R^2} R + \hat{H}_0^L.$$  \hspace{1cm} (A25)

To derive the multichannel analog of Eq. (A3), we note that for the radial integral, we have

$$\int_0^\infty R^2 dR \frac{\psi_n^*(R)}{R} \frac{1}{R} \frac{\partial^2}{\partial R^2} \frac{\psi_n(R)}{R} = \int_0^\infty \psi_n^*(\frac{d}{dR} \psi_n(R)) dR,$$  \hspace{1cm} (A26)

and so we find

$$\left\langle \phi_n | \hat{H}_0 \left| \phi_n \right\rangle \frac{\psi_n}{R} - \frac{\psi_n^*}{R} \left\langle \phi_n | \hat{H}_0 \left| \phi_n \right\rangle \frac{\psi_n}{R} \right\rangle = \frac{\hbar^2}{2 \mu} \delta_{nn'} \Delta V(\psi_n, \psi_{n'}) \big|_{R=\infty}.$$  \hspace{1cm} (A27)

The Kronecker delta $\delta_{nn'}$ arises from the integral over $q$. The multichannel expansion for the zeroth-order wave function with flux-normalized outgoing wave boundary is

$$\Psi^{(+)}_{0,n} = \sum_{n'} \phi_{n'}(q) \frac{\psi_{n'}^{(+)}(R)}{R},$$  \hspace{1cm} (A28)

with, for large $R$,

$$\Psi^{(+)}_{0,n,n'}(R) \approx u_n(R) \delta_{nn'} + v_{n'}(R) \tilde{s}_{n,n'}^{(0)}.$$  \hspace{1cm} (A29)

The incoming and outgoing waves are expressed in spherical Hankel functions of the second and first kind, respectively,

$$u_n(R) = N_n k_n R \psi_n^{(2)}(k_n R) = N \Phi_n^{(2)}(k_n R),$$  \hspace{1cm} (A30)

and the flux normalization is, as mentioned before,

$$N_n = \sqrt{\frac{\mu}{\hbar k_n}}.$$  \hspace{1cm} (A31)

The analog of Eq. (A18) is

$$\left\langle \phi_{n'} | E - \hat{H}_0 | \Delta \Psi_n \right\rangle = \frac{\hbar^2}{2\mu} \sum_{n''} \left\langle \psi_{n'}^{(+)} | \psi_{n''} \right\rangle \Delta \Psi_{n''} \big|_{R=\infty}$$  \hspace{1cm} (A32)

Together with the multichannel analog of Eq. (A10),

$$\left( E - \hat{H}_0 \right) | \Delta \Psi_n \big) = \Delta V \left| \psi_{n'}^{(+)} \right\rangle,$$  \hspace{1cm} (A33)

the MC-DWBA for the $S$-matrix becomes

$$S_{n'n} = s_{n'n}^{(0)} + \frac{2\mu}{\hbar^2} \left( \left| \frac{\psi_{n'}^{(+)} \Delta V | \psi_{n'}^{(+)} \rangle}{\psi_{n'}^{(+)} \Delta V | \psi_{n'}^{(+)} \rangle} \right|_0 \right),$$  \hspace{1cm} (A34)

where the incoming waves $\psi_{n'}^{(+)}$ have radial parts $\psi_{n'}^{(+)}(R) = \psi_{n'}^{(+)}(R)$. The Wronskian in this expression is equal to $2\mu/\hbar$, so the MC-DWBA expression for the $S$-matrix becomes

$$S_{n'n} = s_{n'n}^{(0)} - \frac{i}{\hbar} \left( \left| \frac{\psi_{n'}^{(+)} \Delta V | \psi_{n'}^{(+)} \rangle}{\psi_{n'}^{(+)} \Delta V | \psi_{n'}^{(+)} \rangle} \right|_0 \right).$$  \hspace{1cm} (A35)

Compared to the Cartesian case, Eq. (A21), the sign of the matrix element is different. This is the result of a phase convention: in the Cartesian case, the wave function in Eq. (A14), for $S = 1$, is purely imaginary, whereas in the three-dimensional, single channel case with $L = 0$, the wave function $\Psi^{(+)}$ is real. The extra factor $i$ in the bra and the ket of the matrix element of $\Delta V$ together give another factor $-1$.

For the $K$-matrix boundary conditions in the three-dimensional, multichannel case, we take

$$u_n(k_n R) = N_n k_n R j_l(k_n R) \equiv N_n \sin \left( k_n R - \frac{l\pi}{2} \right),$$  \hspace{1cm} (A36)

$$v_n(k_n R) = -N_n k_n R y_l(k_n R) \equiv N_n \cos \left( k_n R - \frac{l\pi}{2} \right).$$  \hspace{1cm} (A36)
where we included the minus sign in the definition of the irregular waves $v_n$ to get the same phase convention as in the Cartesian case above. Hence, the MC-DWBA expression for the $K$-matrix is

$$K_{n'a'} = K_{n'a'}^{(0)} - \frac{2}{\hbar} \left\{ \psi_{n'a'}^{(K)} \Delta V \psi_{n'a'}^{(K)} \right\}. \quad (A37)$$

Finally, we give the relation between the $S$- and the $K$-matrix,

$$S = \frac{I + iK}{I - iK}, \quad (A38)$$

where $I$ is the identity matrix. The MC-DWBA may give an $S$-matrix that is not perfectly unitary, but as long as the $K$-matrix is symmetric, this last expression will give a unitary $S$-matrix.

**DATA AVAILABILITY**

The data that support the findings of this study are available within the article and its supplementary material.

**REFERENCES**