Ultracold O$_2$ + O$_2$ collisions in a magnetic field: On the role of the potential energy surface

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I. INTRODUCTION

Ultracold molecules play an important role in modern physics due to a large number of promising applications in quantum information, precision spectroscopy, and ultracold chemistry. Optical lattices of ultracold molecules are predicted to be ideally suited for quantum simulation of complex quantum systems and the engineering of new schemes for quantum information storage and processing. On the other hand, creation of a Bose–Einstein condensate (BEC) of molecules may enable studies of Bose-enhanced chemistry. In the context of these studies, molecules must be confined within a trap. For paramagnetic molecules, a magnetic trap is commonly used since molecules in a low-field-seeking state are trappable provided that their translational energy is lower than that of the trap depth. This situation could be achieved by direct cooling methods such as Zeeman slowing, optical Stark deceleration, single-photon cooling, or sympathetic cooling. It might also be possible to cool the molecules toward the ultracold regime by evaporative cooling. As it is well known, this was the successful method for achievement of BEC of atoms.

Molecular collisions are fundamental in this context, as evaporative cooling relies on efficient elastic collisions and, even more crucially, on the ratio $\gamma$ of the probabilities for elastic scattering and spin relaxation which must be very large in order to prevent heating and trap loss. External electromagnetic fields may serve to control the rate of inelastic collisions. Tuning close to a Feshbach resonance has proved to be an extremely fruitful means of controlling atom–atom collisions. Interestingly, it has been recently shown that inelastic collision rates in atom–molecule collisions can be tremendously reduced in the vicinity of a Feshbach resonance controlled by an electric or magnetic field.

While a large amount of work has been carried out for atom–atom and atom–molecule collisions, studies of molecule–molecule collisions in external fields are still scarce. Most clues about these more complex systems have come from atom–molecule studies. Krems and Dalgarno found that the main mechanisms of spin relaxation are energy exchanges mediated by the spin–spin interaction. Volpi and Bohn found that spin depolarization is suppressed when the Zeeman splitting between incident and final states does not exceed the height of the centrifugal barrier in the exit channel. These ideas were confirmed for $^{17}$O$_2$(3$\Sigma_g^-$) + $^{17}$O$_2$(3$\Sigma_g^-$) by Tcherbul et al., who carried out the first accurate computational study involving two diatoms in a magnetic field. In that work, the experimentally derived potential energy surface (PES) of Aquilanti et al. was employed (Perugia PES in what follows). This collisional system is interesting since oxygen has been postulated as a reliable candidate for trapping and cooling and progress in cooling this species has been achieved recently.

The present work builds up along these lines by the investigation of the role played by the PES in O$_2$+O$_2$ collisions in a magnetic field: On the role of the potential energy surface

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collisions in the presence of a magnetic field. It is well known that ultracold atom–atom collisions are very sensitive to the short range of the potential. However, it has been recently shown that, in the presence of inelastic scattering (i.e., atom–molecule collisions), peaks in cross sections around a Feshbach resonance may become suppressed and hence dynamics becomes rather insensitive to the details of the potential. This theory is tested here for a rather anisotropic molecule–molecule system, such as O₂ + O₂, using a recent ab initio PES developed by Bartolomei et al. In this potential, electronic correlation is included by means of a high-level supermolecular method in the short range, whereas long-range interaction coefficients have been obtained from first principles as well. It is worthwhile to mention that inelastic rate coefficients obtained with this PES have proved to be highly consistent with measurements of the evolution of rotational populations along supersonic expansions in the temperature range 10 ≤ T ≤ 34 K. By comparing present scattering calculations with previous ones using the Perugia PES (Ref. 25) and with some additional test modifications of the ab initio PES, the effect of the potential on the cold and ultracold dynamics has been assessed.

This paper is organized as follows. In Sec. II, a summary of the theory for the scattering between two identical 3Σ molecules is given. Details specific to the 17O₂ − 17O₂ system are provided in Sec. III and in Sec. IV, results are reported and discussed. A concluding remark is given in Sec. V.

II. THEORY

We give a summary of the theory—recently developed by Tscherbul et al.—for the scattering of two 3Σ identical rigid rotor molecules in the presence of a magnetic field. Diatom–diatom Jacobi coordinates are used in a space-fixed (SF) frame, including the vector joining the centers of mass of the molecules a and b, R̂, and the intramolecular unit vectors, ̂r_a and ̂r_b. Intramolecular distances are fixed to the molecular equilibrium distance, r_a = r_b = r_e. The Hamiltonian of the system can be written as

\[ \hat{H} = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hat{l}^2}{2\mu R^2} + V(R, \hat{r}_a, \hat{r}_b) + \hat{H}_a + \hat{H}_b, \]

where atomic units are used (\( \hbar = 1 \)), \( \hat{l} \) is the orbital angular momentum, \( \mu \) is the reduced mass, and \( V \) is the interaction potential or PES. The internal Hamiltonian of the 3Σ molecule \( \hat{H}_a(a = b) \) is given, within the rigid rotor approximation, by

\[ \hat{H}_a = B_a \hat{J}_a^2 + 2\mu_B B \cdot \hat{s}_a + \gamma_{sr} \hat{\mu}_a \cdot \hat{s}_a + \frac{2}{\lambda_{ss}} \sqrt{ \frac{4\pi}{5} } \sum_q Y_2^q(\hat{r}_a) [\hat{\delta}_a \otimes \hat{s}_a]_q^{(2)}, \]

where \( \hat{\mu}_a \) is the angular momentum associated with \( \hat{r}_a \), \( B_a \) is the rotational constant, \( \mu_B \) is the Bohr magneton, \( B \) is the external magnetic field, and \( \hat{s} \) is the electron spin.

The last two terms in Eq. (2) correspond to the spin-rotation and spin–spin interactions, parameterized by \( \gamma_{sr} \) and \( \lambda_{ss} \), respectively. Hyperfine and intermolecular magnetic dipole interaction are neglected (see Ref. 28 for details). It is worth mentioning that, while the magnetic dipole interaction plays a very small role (≈1% \) in O₂ + O₂ at zero magnetic field, it can be very important in other systems, as recently shown in Refs. 36 and 37.

The total wavefunction is expanded in a basis set of SF uncoupled and symmetry-adapted functions

\[ \psi^{M_{re}} = \frac{1}{R} \sum_{\tau_a \geq \tau_b \geq l,m} u^{M_{re}}(\tau_a, \tau_b, l, m) \phi^{M_{re}}(\hat{r}_a, \hat{r}_b), \]

with

\[ \phi^{M_{re}} = \frac{1}{\sqrt{2(1 + \delta_{\tau_a,\tau_b})}} \left[ (\tau_a \tau_b) + \eta \epsilon |\tau_a \tau_b| \right] |m\rangle, \]

where \(|m\rangle\) is a spherical harmonics and where \(|\tau_a\rangle\) represents an uncoupled function of the \( \alpha \) monomer

\[ |\tau_a\rangle = |n_a m_{n_a}| |s_a m_{s_a}. \]

The basis of Eq. (4) are a well-ordered set with \( \tau_a \geq \tau_b \) that are normalized eigenfunctions of the operator permuting the identical molecular skeletons \( (\hat{P}: \hat{r}_a \rightarrow \hat{r}_b; \hat{r}_b \rightarrow \hat{r}_a; \hat{R} \rightarrow -\hat{R}) \), with eigenvalue \( \eta \). These basis functions are also eigenfunctions of spatial inversion \( (\hat{E}^* \rightarrow -\hat{E}^*; \hat{r}_a \rightarrow -\hat{r}_a; \hat{r}_b \rightarrow -\hat{r}_b; \hat{R} \rightarrow -\hat{R}) \) with eigenvalue \( \epsilon = (-1)^{\tau_a + \tau_b + l}. \)

In addition to these symmetries, the Hamiltonian commutes with the SF \( z \) axis component of the total angular momentum, so that for a given value of this projection, \( M \), basis functions in Eq. (3) must satisfy

\[ m_{n_a} + m_{n_b} + m_{s_a} + m_{s_b} + m_l = M. \]

Substitution of Eq. (3) into the Schrödinger equation leads to the set of close-coupled equations for the radial coefficients:

\[ \left[ \frac{1}{2\mu} \frac{d^2}{dR^2} - \frac{l(l + 1)}{2\mu R^2} + E \right] u^{M_{re}}(\tau_a, \tau_b, l, m) \]

\[ \sum_{\tau'_a \geq \tau'_b \geq m'_l} \langle \phi^{M_{re}}(\tau_a, \tau_b, l, m) | (\hat{V} + \hat{H}_a + \hat{H}_b) | \phi^{M_{re}}(\tau'_a, \tau'_b, l', m') \rangle H^{M_{re}}(\tau'_a, \tau'_b, l', m'), \]

where \( E \) is the total energy. It must be pointed out that the asymptotic Hamiltonian \( \hat{H}_a + \hat{H}_b \) is not diagonal in the basis \( \phi^{M_{re}}(\tau_a, \tau_b, l, m) \) due to the spin-rotation and spin–spin terms, and matrix elements of these terms are given in Eqs. (14) and (16) of Ref. 23, respectively. On the other hand, potential matrix elements are given as a sum of a direct and an exchange coupling terms:

\[ \langle \phi^{M_{re}}(\tau_a, \tau_b, l, m) | V | \phi^{M_{re}}(\tau'_a, \tau'_b, l', m') \rangle = \frac{1}{[(1 + \delta_{\tau_a,\tau'_a})(1 + \delta_{\tau_b,\tau'_b})]^{1/2}} \times \left[ \langle \tau_a \tau_b | l, m \rangle | V | \tau'_a \tau'_b \rangle (l', m') \right] + \eta \epsilon \langle \tau_a \tau_b, l, m | V | \tau'_a \tau'_b, l', m' \rangle. \]
molecules, $S = 0, 1, 2$, and can be represented as
\[ V(\vec{R}, \vec{p}_a, \vec{p}_b) = \sum_{S=0}^{2} \sum_{M_S=-S}^{S} V_S(\vec{R}, \vec{p}_a, \vec{p}_b)|(SM_S)\rangle(SM_S), \]
(9)
where $M_S$ is the projection of the total spin, $M_S = m_s + m_{s_b}$. We use this representation in order to include directly the singlet, triplet, and quintet \textit{ab initio} PESs of Ref. 32 (an alternative approach was followed in Ref. 25 since the Perugia PES is given as a sum of a spin-independent and a spin-dependent contribution26). In this way, matrix elements of Eq. (8) can be further developed as
\[ (\tau_a | \tau'_a | V | \tau'_b | m_f) = \delta_{M_f M_i} \sum_{S=0}^{2} (2S + 1) \begin{pmatrix} 1 & 1 & S \end{pmatrix} \begin{pmatrix} n_a m_s n_b m_{s_b} \end{pmatrix} \times |V_S n'_a m_n' n'_b m_{n_b}' l_m l_f \rangle, \]
(10)
where $(::)$ are 3-3 symbols. An explicit expression for $(n_a m_s n_b m_{s_b} | V | n'_a m_n' n'_b m_{n_b}' l_m l_f)$ is given in Eq. (18) of Ref. 25.

Close-coupled equations [Eq. (7)] are solved by means of a log-derivative method29,30 and using the basis set of Eq. (4) in which, as mentioned above, the asymptotic Hamiltonian is not diagonal. In order to set scattering boundary conditions and thus, obtain the scattering S-matrix, it is necessary to transform to a new basis set \( \psi'_{l_m l, m_l, m_i} \) giving the eigenstates of the fragments. For each $l, m_l$ block:
\[ \hat{H}_a + \hat{H}_b \psi'_{l_m l, m_l, m_i} = (\varepsilon_{l_m} + \varepsilon_{l_i}) \psi'_{l_m l, m_l, m_i}, \]
(11)
where $\varepsilon_{l_m}$ is the Zeeman fine structure energy level of molecule $\alpha$. A unitary transformation of the log-derivative matrix onto the new basis is performed at the end of the calculation, and then scattering S-matrices and transition T-matrices are obtained in a standard way.25 The integral cross section for a transition $|\alpha, \eta, \xi_\alpha \rangle \rightarrow |\beta, \eta', \xi_\beta \rangle$ within a given $(M, \eta, \epsilon)$ block is finally given as
\[ \sigma_{\alpha \rightarrow \beta}^{M \eta \epsilon} = \pi \left(1 + \delta_{\xi_\alpha \xi_\beta} \right) \sum_{l_m, l_f} |T_{\alpha \rightarrow \beta}^{M \eta \epsilon} l_m l_f |^2, \]
(12)
where $T$ is the transition matrix and $k^2_{\alpha \rightarrow \beta} / (2 \mu) = E - \varepsilon_{\alpha} - \varepsilon_{\beta}$ is the translational energy of the initial channel. In obtaining Eq. (12), integration of the differential cross section has been restricted over half-space for final states satisfying $\xi' = \xi$ (see Ref. 25). This is equivalent to dividing the cross sections integrated over full-space by two to avoid double counting when the state of the outgoing molecules is the same.41,42

### III. COMPUTATION DETAILS

We consider collisions between \textsuperscript{17}O\textsubscript{2}(\textsuperscript{3}Σ\textsubscript{g}\textsuperscript{−}) identical molecules as in the work of Tschernbul et al.25 The \textsuperscript{17}O isotope was chosen because field-free calculations of Avdeenkov and Bohn showed that \textsuperscript{17}O\textsubscript{2} is a much better candidate for ultracold studies than the more abundant \textsuperscript{16}O\textsubscript{2} isotopologue.28 The asymptotic Hamiltonian of Eq. (2) is parameterized by means of accurate \textsuperscript{17}O electronic spectroscopic constants:43 $\beta = 1.353$ cm\textsuperscript{−1}, $\gamma_x = -0.00396$ cm\textsuperscript{−1}, and $\lambda_x = 1.985$ cm\textsuperscript{−1}. The three lowest states of the $n = \text{even}$ manifold (compatible with molecules in the stretched nuclear spin state $M_I = I = 5$ [Ref. 28]) are given in Table I for a typical value of the magnetic field. Dependence with magnetic field of the combined $|\xi_\alpha, \xi_\beta \rangle$ asymptotic states is depicted in Fig. 1. In this work, we focus on the initial state $|\xi_\alpha, \xi_\beta \rangle = |3, 3 \rangle$, i.e., both molecules are, prior to interaction, in their lowest \textit{hfs} state. Elastic and inelastic integral cross sections are obtained for translational energies ranging from $10^{-8}$ to 0.05 K. As we are dealing with collisions between identical (composite) bosons, calculations are restricted to the $\eta = +1$ block (the role of nuclear spin can be ignored, as explained in detail in Ref. 28). Note also that to study processes involving identical internal states [Eq. (4)], calculations are constrained to the $\epsilon = +1$ parity (only even $l$’s in the wavefunction expansion).

The intermolecular interaction is given by the global \textit{ab initio} PES of Bartolomei et al.,32 specifically, the one referred in that work as CC-PT2 PES. Singlet, triplet, and quintet ($S = 0, 1, 2$) potentials are given32 by the spherical harmonic

![FIG. 1. Internal energies of \textsuperscript{17}O\textsubscript{2}(\textit{L}) and \textsuperscript{17}O\textsubscript{2}(\textit{Q}) as functions of magnetic field. In this work, molecules are considered to be initially in their \textit{hfs} states $|\xi_\alpha, \xi_\beta \rangle = |3, 3 \rangle$. Open and closed symbols indicate critical values of the field for which $d$ and $g$ barriers, respectively, become open for the different outgoing channels. Note also that calculations of Fig. 4 refer to the \textit{hfs} state $|1, 1 \rangle$.](https://journals.aip.org/doi/10.1063/1.3611103)
of the four identical nuclei). The radial coefficients were obtained by means of quadratures of the supermolecular \( ab \) initio energies over the angular variables, obtaining a total of 29 coefficients for the quintet PES and 27 for the singlet and triplet ones. The PESs are extended asymptotically for translational energies lower than \( 10^4 \) a.u., scale length \( R_{vdW} \), and energy \( E_{vdW} \) of the analytical \( vdW \) theory (Ref. 46), and height of the \( d \)-wave centrifugal barrier. \( B_{\text{min}} \) is the critical magnetic field for which the \( [3,3] \rightarrow [3,1] \) Zeeman splitting becomes larger than the \( d \)-wave barrier.

expansion,

\[
V_S(\vec{R}, \hat{r}_a, \hat{r}_b) = \left( 4\pi \right)^{3/2} \sum_{\lambda_a, \lambda_b} V_{S}^{\lambda_a, \lambda_b}(R) A_{\lambda_a, \lambda_b}(\vec{R}, \hat{r}_a, \hat{r}_b),
\]

where \( A_{\lambda_a, \lambda_b} \) is given as a combination of spherical harmonics and \( \lambda_a, \lambda_b \), and \( \lambda \) are even integers (due to the symmetry of the four identical nuclei). The radial coefficients \( V_{S}^{\lambda_a, \lambda_b}(R) \) were obtained by means of quadratures of the supermolecular \( ab \) initio energies and Perugia PES, which comprises just four

| Table II. Parameters associated with the long-range behavior of the \( ab \) initio and Perugia potentials: isotropic \( vdW \) coefficient \( C_{6}^{\text{iso}} \), scale length \( R_{vdW} \), and energy \( E_{vdW} \) of the analytical \( vdW \) theory (Ref. 46), and height of the \( d \)-wave centrifugal barrier. \( B_{\text{min}} \) is the critical magnetic field for which the \( [3,3] \rightarrow [3,1] \) Zeeman splitting becomes larger than the \( d \)-wave barrier. |
|-----------------|-----------------|-----------------|
|                 | \( ab \) initio  | Perugia         |
| \( C_{6}^{\text{iso}} \) (a.u.) | 62.39           | 88.70           |
| \( R_{vdW} \) (a.u.)         | 22.17           | 24.21           |
| \( E_{vdW} \) (mK)          | 10.4            | 8.7             |
| \( E_{0}(l = 2) \) (mK)     | 14.7            | 12.3            |
| \( B_{\text{min}} \) (G)    | 55              | 46              |

(from 4.5 to 40.8 \( a_0 \)) with a fixed short step (0.04 \( a_0 \)), whereas the Airy propagator of Ref. 40 is used for the long-range region (from 40.8 to 202. \( a_0 \)) with a variable step size (the ratio between adjacent step sizes being 1.05). Comparing with the original code of Tscherbul et al., where only the log-derivative propagator was used, we found that the errors are less than 0.5% while the new propagation is about ten times faster due to the smaller number of integration steps as well as the use of the computationally less expensive Airy propagator.

The total wavefunction is expanded using a basis set comprising three rotational levels \( (n_a, n_b, J_a, J_b, \lambda) \) and four partial waves \( (l = 0, 2, 4, 6) \) and four

\[ \langle 3,3|\lambda_a,\lambda_b|3,3\rangle \]

were obtained by means of quadratures of the supermolecular \( ab \) initio energies and Perugia PES, which comprises just four radial terms (for each multiplicity) derived from a multiproperty fitting analysis. To give a flavor of the similarities/differences between the two PES considered, we present in Sec. IV, we present a comparison with calculations using the Perugia PES, which comprises just four radial terms (for each multiplicity) derived from a multiproperty fitting analysis. To give a flavor of the similarities/differences between the two PES considered, we present in Fig. 2 the dependence with the intermolecular distance of the potential matrix elements among the \( I / s \) state \( [3,3] \) and the \( (1s^2) \) relaxation channel \( [3,1] \). These matrix elements are relevant to the mechanisms proposed by Krems and Dalgarno and by Volpi and Bohn. Note that for initial states approaching an \( s \) wave, conservation of \( M \) forbids \( s \) waves in the spin relaxation channels (see Eq. (6) and Ref. 24). It can be seen that there are some quantitative differences in the coupling as well as in the long-range behavior. A comparison of properties related to the long-range behavior is summarized in Table II.

Cross sections are computed using the code developed by Tscherbul et al., modified by us to include the hybrid log-derivative/Airy propagator of Alexander and Manolopoulos. Related routines were taken from the MOLSCAT code. In this way, the log-derivative propagator of Manolopoulos is used in the strongly coupled region

IV. RESULTS AND DISCUSSION

We present first the results concerning the magnetic-field dependence at very low energies and, in a subsequent section, we report those related to the translational energy dependence, including the transition from the ultracold to the cold regimes.

A. Magnetic-field dependence at 1 \( \mu \)K

The magnetic-field dependence of the cross sections for the \( I / s \) state \( [3,3] \) at 1 \( \mu \)K is summarized in Fig. 3 [panels (a) and (b)], where results obtained using the \( ab \) initio and Perugia PES are compared. In Fig. 3(c) we report the elastic-to-inelastic ratio, \( \gamma \), more specifically, the ratio between the elastic cross section and those inelastic ones leading to untrapped states: \( [\zeta_1', \zeta_2'] = [3,1], [2,2], [2,1], \) and \( [1,1] \). Note that new calculations with the Perugia PES were performed using the same basis set as with the \( ab \) initio PES (there are
some quantitative changes between present calculations and those given in Fig. 3 of Ref. 25 where a smaller basis was employed). There are various noticeable differences between the two PESs. On the one hand, elastic and inelastic cross sections calculated with the \textit{ab initio} PES are much larger than those using the Perugia PES and, in addition, they exhibit more marked Feshbach resonance structures [Figs. 3(a) and 3(b)]. On the other hand, although there are large variations of the elastic-to-inelastic ratio with the magnetic field, it can be seen that both PESs produce values which, on average, are of the same order of magnitude. The cases of very low fields ($B < 50$ G), where $\gamma$ is much larger for the Perugia PES, and around 1000 G, where the value from the \textit{ab initio} PES becomes very large, are discussed in more detail below.

We discuss first the background behavior of the cross sections of Fig. 3. The elastic cross sections correspond to a background scattering length, $a_{bg}$, of about 118 and 32 $a_0$, for the \textit{ab initio} and Perugia PESs, respectively ($a_{bg}$ is the modulus of the complex scattering length\cite{30}). These quantities are larger than the scattering lengths purely due to the vdW potential\cite{30} $\overline{a}$, of 22 and 24 $a_0$, respectively. The particularly large value of the elastic cross section using the \textit{ab initio} PES can be explained by existence of a close quasibound state varying with magnetic field at the same rate than the entrance channel. Regarding inelastic cross sections, the one from the \textit{ab initio} PES is on average about ten times larger than the result corresponding to the Perugia PES. This difference can be qualitatively rationalized by resorting to the analytic van der Waals theory\cite{46,47}, which takes the solutions of the vdW potential\cite{48} as the reference for the multichannel quantum defect theory\cite{49}.

A key parameter in that approach is the short-range squared amplitude of the entrance channel wavefunction, which near threshold is proportional to\cite{46}

$$\lim_{\kappa_0 \to 0} C_{bg}(\kappa_0)^{-2} = \kappa_0 \overline{a} \left[ 1 + \left( 1 - \frac{a_{bg}}{\kappa_0} \right)^2 \right],$$

\(k_0\) being the wavenumber of the incoming channel. Since inelastic cross sections are proportional to $C_{bg}(\kappa_0)^{-2}$,\cite{49} Eq. (14) implies that the value of $a_{bg}$ affects the threshold behavior of the inelastic cross sections. It follows, then, that the very large inelastic cross sections calculated with the \textit{ab initio} PES (compared to those corresponding to the Perugia PES) are explained by the magnitude of the corresponding background scattering length. Within this framework, one can expect that the elastic-to-inelastic ratio becomes less sensitive to $a_{bg}$ than the cross sections themselves, since both elastic and inelastic cross sections are approximately proportional to $a_{bg}^2$. This is the result of Fig. 3(c), where the average value of $\gamma$ is about the same for both potentials.

We now turn to discuss the resonant structures of Fig. 3. At this point, it is convenient to mention the work of Hutson\cite{31} who analyzed the threshold behavior of Feshbach resonances in the presence of inelastic scattering. He found that—in contrast to the case of a pure elastic scattering—resonance peaks may be significantly suppressed and, in this way, the collisional process may become insensitive to the details of the potential. With this in mind, the profiles obtained in Fig. 3 are rather unexpected given the considerable anisotropy of the O$_2$–O$_2$ interaction. In connection with this issue, let us digress for a while and study the resonance patterns for a purely elastic scattering event, as is the case of the magnetic-field dependence of the lowest high-field-seeking (hfs) state [1, 1] (see Fig. 1). The result for the \textit{ab initio} PES at 1 $\mu$K, using a reduced basis ($n_{\text{max}} = 4$, $l_{\text{max}} = 4$), is shown in Fig. 4 and can be directly compared with Fig. 4 of Ref. 25. For both PESs, a high density of very pronounced resonances is obtained. For the \textit{ab initio} PES there is a slightly larger number of peaks, and some of them are wider. Also, the baseline of the cross section computed using the \textit{ab initio} PES is much larger than that using the Perugia PES, as occurs for the hfs state. A similar density of quasibound states is expected when the entrance channel is the hfs state but presence of inelastic channels substantially modify the resonance lineshapes.\cite{31} To show this, it is convenient to write down the behavior of the $S$ matrix in the neighborhood of an isolated resonance,\cite{31,50}

$$S_{jk}(E) = S_{jk}^{bg} - i \frac{g_{ji} g_{kj}}{E - E_r + i \Gamma_E/2},$$

where $k$ and $j$ are the incoming and outgoing channels, respectively, $S_{jk}^{bg}$ is the background $S$ matrix, $E$ is the total energy, $E_r$ is the resonance position, $\Gamma_E$ is the resonance width, and (complex) $g_{ji}$ involve couplings between resonance and channel $i$ wavefunctions,\cite{51} such that the partial width for

![FIG. 3. Magnetic-field dependence for collisions of $^{17}$O$_2 + ^{17}$O$_2$ in the initial $f$s state $|3, 3\rangle$ and translational energy of 1 $\mu$K. (a) Elastic cross sections; (b) total inelastic cross sections; and (c) ratio $\gamma$ between elastic and inelastic (untrapping) cross sections. Blue and red colors correspond to using the \textit{ab initio} (Ref. 32) and the Perugia (Ref. 26) PESs, respectively.](image-url)
Eq. (14). Hence, if elements, as they become proportional to the square root of channel $i$ is given as $\Gamma_{Ei} = |g_{Ei}|^2$ and $\Gamma_E = \sum_i \Gamma_{Ei}$. A key point in Hutson’s argument is that $g_{Ek}$ elements are proportional to the square root of the incoming channel wavenumber $k_0^{1/2}$. Then, as $k_0$ decreases and if the resonant state is also coupled to inelastic channels, the radius of the circle described by $S_{jk}$ drops to zero and peaks in cross sections become significantly suppressed.31 The analytical vdW theory gives a more detailed threshold behavior of the $g_{Ek}$ elements, as they become proportional to the square root of Eq. (14). Hence, if $a_{bg}$ is sufficiently large, $g_{Ek}$ will tend to its threshold value (zero) rather slowly, and as a consequence, more pronounced peaks in the cross sections can be obtained. This explains why we find a marked resonance structure, especially for the ab initio PES. Nevertheless, as noted in Ref. 31, a relatively large ratio between elastic and inelastic partial widths is also needed in order to obtain pronounced resonance profiles. It is reasonable to expect that, among all the quasi-bound states that should be crossing the $I_{fs}$ state, only some of them will have particularly large elastic partial widths, so only a few marked resonance features will “survive,” as in fact it occurs (Fig. 3).

We have just seen that a large $a_{bg}$ enhances the short-range couplings between the resonance and the incoming wavefunctions. In this situation the dynamics must become very sensitive to the short-range region of the potential. In order to study the role played by the short-range versus the long-range features of the intermolecular potential, we have performed a test calculation where the long-range anisotropy of the potential is switched off. To this end, the ab initio PES has been modified by imposing, for $R > 19 a_0$, an exponential decay of all radial terms of Eq. (13) except the isotropic one $(\lambda_a, \lambda_b, \lambda) = (000)$. The new cross sections are compared with those corresponding to the correct long-range behavior in Fig. 5. This figure clearly shows that the resonance structure is rather insensitive to the long-range anisotropy of the interaction and, therefore, short-range couplings must be playing a dominant role.

Finally, it is interesting to note from Fig. 3(b) that, for the ab initio PES, there is a significant suppression of inelastic scattering for magnetic fields ranging from 750 to 1500 G. This feature must be related with the prominent resonance at about 600 G and it must be due to interferences between the background and resonant $S$ matrices leading to asymmetric line-shapes of the state-to-state cross sections.52 Note that this reduction entails a considerable increase of the ratio $\gamma$ for a wide range of magnetic fields. A similar behavior (with an even larger suppression of inelastic scattering) has been found in $^4$He + $^{16}$O$_2$ magnetic Feshbach resonances.22

Analogously, it is also worth mentioning that, for the results corresponding to the ab initio PES, the elastic scattering on the left-hand-side of the resonance at about $B = 30$ G is suppressed. This feature, already present in Fig. 3, can be more clearly seen in Fig. 5, where the elastic cross section becomes very small around 10 G. In this case, the corresponding ratio $\gamma$ becomes much smaller than expected (from the well known effect of suppression of inelastic scattering due to centrifugal barriers34,25,28).

B. Translational energy dependence

In Fig. 6, dependence of the cross sections with kinetic energy is given for several selected values of the magnetic field. In agreement with predictions based on the analytical vdW theory,46 two very different regimes are noticed for energies larger or smaller than $E_{vdW} \approx 10$ mK (see Table II). For the higher energy range, elastic and inelastic cross sections exhibit a weak dependence with the field, the ones obtained using the Perugia PES being larger than their ab initio counterparts, in consistency with previous studies at higher energies.41 For energies lower than the crossover ($E_{vdW}$), cross sections become more dependent on the magnetic field. This is mainly due to the effect of the resonances in the ultracold regime, but in the case of the Perugia PES, suppression of inelastic cross sections at low fields (due to the centrifugal barriers25,28) also plays a role.
FIG. 6. Translational energy dependence of the collisional processes for the \( ^3\text{P}_0 \) state \( \text{O}_2 + \text{O}_2 \) collisions \( \text{J. Chem. Phys.} \) 10 mK in the calculation using the elastic-to-inelastic ratio has been obtained between 1 and 5 G and between 1 and 10 mK, discussed above (Fig. 3).

A more detailed study of the cross sections calculated with the \textit{ab initio} PES for low values of the field \( (B \leq 50 \text{ G}) \) is given in Fig. 7. An impressive dependence with \( B \) is noticed for energies just below 10 mK. Between 1 and 10 mK, complicated resonance structures are seen which are particularly acute for the elastic cross section. These features are related to the prominent resonance around 30 G at much lower energies (reported in Fig. 3 and more clearly seen in Fig. 5). In other words, they are expressions—at several different energies and magnetic fields—of the same quasibound state. For instance, note the resemblance between the asymmetric line shapes of the elastic cross section at \( B = 1 \) and 5 G and between 1 and 10 mK [Fig. 7(a)], with the magnetic-field dependence at much lower energies for fields \( B < 30 \text{ G} \), as shown in Fig. 5. A detailed tracking of these resonances would involve non-trivial lineshape fittings and has not been attempted here. On the other hand, it should be noted that, for the range of magnetic fields of Fig. 7 and up to translational energies of at least 1 mK, spin-changing collisions should be suppressed due to existence of centrifugal barriers in all outgoing channels.

In Fig. 7(b) it can be seen that, except for the lowest value of \( B \) (1 G), such a suppression does not occur, in contrast with the results using the Perugia PES [see Ref. 25 and Fig. 6(b)]. This must be due to a significant tunneling through the centrifugal barriers for energies/fields close to the resonance. Consequently, the ratios \( \gamma \) are particularly small for this range of fields [Fig. 7(b)].

A further analysis of the sensitivity of the elastic-to-inelastic ratio to the details of the PES has been performed. We have artificially modified the anisotropy of the present \textit{ab initio} PES by multiplying all the terms in the spherical harmonic expansion [Eq. (13)]—except the isotropic ones—by a factor \( \beta \) ranging from 0.98 to 1.02. In Fig. 8 we show the results for different translational energies and magnetic fields. It can be seen that, while for 20 mK there is not a strong variation of \( \gamma \) with \( \beta \), for lower energies (1 mK and 1 \mu K), this ratio changes tremendously with the anisotropy of the potential. In the new calculations (\( \beta = 0.98 \) and 1.02), no nearby resonances appear for the energies/fields considered and hence, results are “more standard,” i.e., very large values of \( \gamma \) are now attained for low values of the field (\( B < 50 \text{ G} \)), in agreement with the expected suppression of inelastic scattering, but smaller \( \gamma \)’s are obtained for \( B = 1000 \text{ G} \). However, note that, contrarily to a first order perturbation theory, the largest ratios are obtained with the most anisotropic PES (\( \beta = 1.02 \)).
FIG. 8. Study of the sensitivity of the elastic-to-inelastic ratio γ to the anisotropy of the \textit{ab initio} PES. All terms of the spherical harmonic expansion are multiplied by β except the isotropic one. The effect is shown for different translational energies and magnetic fields.

V. CONCLUDING DISCUSSION

We have performed a detailed study of cold and ultracold molecule–molecule collisions in the presence of a magnetic field for a system with a significant anisotropy such as O$_2$+O$_2$. A thorough comparison has been made between a high quality \textit{ab initio} PES and previous studies$^{25}$ where a different PES was used. Several interesting findings have emerged from this approach regarding the anisotropy as well as the relative influence of long and short components of the interaction. For the \textit{ab initio} PES, a large background scattering length gives rise to pronounced resonance structures in the ultracold regime (translational energies < 10 mK). As a consequence, the ratio between elastic and inelastic cross sections, γ, is very dependent on the magnetic field as well as on the short-range anisotropy of the PES. Therefore, quantitative predictions for this important parameter become rather risky. However, and as a general trend, we can indicate that high values of γ could be achieved in the vicinity of asymmetric Fano resonances, or for low fields, B < 50 G. Note that the maximum temperature that can be held in a trap with such a depth would be of about 1 mK.$^{25,53}$

A key issue is the large density of quasibound states of the O$_2$ + O$_2$ system, best illustrated in the magnetic-field dependence of the elastic cross sections of the lowest high-field-seeking state. In view of this, having obtained a large background scattering length does not seem a rare event. Present behavior might be characteristic of a range of molecule–molecule systems as well, that is to say, as the number of degrees of freedom increases, a larger density of quasibound states, including near threshold resonances, can be expected.$^{54}$ which in turn makes dynamics richer. Very recently, Suleimanov and Krems$^{55}$ have proposed an efficient method for locating Feshbach resonances in external fields. The new method could be very useful for the comparison of spectral patterns obtained from different potentials or between different molecular systems.

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