Nonadiabatic Electronic Energy Transfer in the Chemical Oxygen–Iodine Laser: Powered by Derivative Coupling or Spin–Orbit Coupling?

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ABSTRACT: Derivative couplings near a conical intersection and spin–orbit couplings between different spin states are known to facilitate nonadiabatic transitions in molecular systems. Here, we investigate a prototypical electronic energy transfer process, \( \text{I}(2\Sigma^+) + O_2(a^1\Delta_g) \rightarrow \text{I}(2\Sigma^+) + O_2(X^2\Sigma_g^-) \), which is of great importance for the chemical oxygen–iodine laser. To understand the nonadiabatic dynamics, this multistate process is investigated in full dimensionality with quantum wave packets using diabatic potential energy surfaces coupled by both derivative and spin–orbit couplings, all determined from first principles. A near quantitative agreement with structural, energetic, and kinetic measurements is achieved. Detailed analyses suggest that the nonadiabatic dynamics is largely controlled by derivative coupling near conical intersections, which leads to a small effective barrier and hence a slightly positive temperature dependence of the rate coefficient. The new results should extend our understanding of energy transfer, provide a quantitative basis for numerical simulations of the chemical oxygen–iodine laser, and have important implications in other electronic energy transfer processes.

Since its first demonstration more than 40 years ago,\(^8,9\) the chemical oxygen–iodine laser (COIL) has been optimized to deliver up to megawatt level continuous wave power output, finding many important applications, such as nuclear fusion.\(^7\) This near-infrared gas phase laser takes advantage of the 1315 nm emission of spin–orbit (SO) excited iodine atoms (\( \text{I}(2\Pi_{1/2}) \)) to their ground state counterpart (\( \text{I}(2\Pi_{3/2}) \)). The preparation of excited iodine atoms is achieved by efficient near-resonant electronic energy transfer from electronically excited oxygen molecules in the following process

\[
\text{I}(3\Sigma^+) + O_2(a^1\Delta_g) \rightarrow \text{I}(2\Pi_{3/2}) + O_2(X^2\Sigma_g^-) \quad \Delta U = -279 \text{ cm}^{-1} \tag{R1}
\]

To better understand its mechanism and to further optimize the laser, the kinetics of R1 (and its inverse process) has been investigated experimentally at room temperature\(^4,5,10\) and more recently at the laser operating temperature of 150 K.\(^5,10\) Interestingly, the rate coefficient \( k_r \) is large (\( \sim 10^{-16} \text{ cm}^3 \text{ s}^{-1} \)) and has a slightly positive temperature dependence between 150 and 300 K. These experimental results have stimulated kinetic modeling,\(^11\) but the ultimate understanding requires microscopic dynamics on \textit{ab initio} potential energy surfaces (PESs).\(^12,13\) So far, however, a quantitative characterization of the energy transfer kinetics and dynamics from first principles has yet to be achieved.

Apart from its relevance to COIL, R1 is also a prototype for understanding electronic energy transfer, which differs significantly from energy transfer involving molecular rotation and vibration. The key issue here is the breakdown of the Born–Oppenheimer approximation, which allows transitions between different electronic states in molecular systems. Nonadiabatic transitions between different spin states in such spin-forbidden reactions\(^14\) are due to SO couplings, a relativistic effect.\(^15,16\) Furthermore, nonadiabatic processes may also be possible for systems involving electronic degeneracies such as conical intersections (CIs), which manifest as \( N \)–2–dimensional seams between electronic states, where \( N \) is the dimensionality of the nuclear configuration space.\(^17–19\) Nonadiabatic transitions between two adiabatic states in the same spin manifold coupled by a CI are enabled by derivative couplings, stemming from changes of electronic wave functions with respect to nuclear motion. In R1, both SO and derivative couplings are present,\(^12,13\) making it an interesting and unique system to study nonadiabatic dynamics.

A comprehensive understanding of the kinetics and dynamics of R1 requires an accurate characterization of both the electronic structure and nuclear dynamics. Due to the strong SO coupling of the heavy iodine atom, the electronic configuration of iodine-containing molecules is quite complex.\(^20\) The nuclear dynamics

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involving nonadiabatic transitions are also challenging, as a quantum treatment is needed.\textsuperscript{21} Earlier theoretical models for R1 by Morokuma and co-workers have relied on a semiclassical trajectory surface hopping (TSH) treatment of nonadiabatic transitions among several relevant PESs obtained at the complete active space with the second-order perturbation theory (CASPT2) level of theory.\textsuperscript{12,13} These diabatic PESs and their couplings were expressed in two dimensions with the O–O bond length fixed at its equilibrium. While the experimental result at 150 K was reproduced, their theoretical work predicted a decay of $k_2$ with increasing temperature.\textsuperscript{15} This disagreement with experiment was attributed to an over-estimation of the attractive van der Waals interaction in the reactant channel of R1. Because of the many approximations involved in these studies, however, it is not obvious if the failure in reproducing the experimental trend is due to the inaccurate electronic structure calculations, the reduced dimensional model, or the semiclassical treatment of the dynamics. Furthermore, it is not clear which nonadiabatic coupling, SO or derivative, is dominant.

In this Letter, we report a thorough investigation of R1 by performing full-dimensional nonadiabatic quantum scattering calculations on new and much more accurate coupled PESs. There are two major aims here. The first is to attempt a quantitative reproduction of the experimental rate coefficient and its temperature dependence, and the second is to gain insights into the dynamics by identifying key nonadiabatic pathways.

The electronic structure calculations for constructing the diabatic potential energy matrix (DPEM) of the IO₂ system were performed by Morokuma and co-workers with reliance on a semiclassical trajectory surface hopping (TSH) treatment of nonadiabatic transitions among several relevant PESs obtained at the complete active space with the second-order perturbation theory (CASPT2) level of theory.\textsuperscript{12,13} These diabatic PESs and their couplings were expressed in two dimensions with the O–O bond length fixed at its equilibrium. While the experimental result at 150 K was reproduced, their theoretical work predicted a decay of $k_2$ with increasing temperature.\textsuperscript{15} This disagreement with experiment was attributed to an over-estimation of the attractive van der Waals interaction in the reactant channel of R1. Because of the many approximations involved in these studies, however, it is not obvious if the failure in reproducing the experimental trend is due to the inaccurate electronic structure calculations, the reduced dimensional model, or the semiclassical treatment of the dynamics. Furthermore, it is not clear which nonadiabatic coupling, SO or derivative, is dominant.

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The electronic structure calculations for constructing the diabatic potential energy matrix (DPEM) of the IO₂ system were carried out using the MOLPRO package.\textsuperscript{22} In the first step, spin-free adiabatic energies of low-lying electronic states were calculated, using the internally contracted multireference configuration interaction method with the Davidson correction (ic-MRCI+Q).\textsuperscript{23} The correlation-consistent polarized valence quadruple-ζ basis set (cc-pVQZ)\textsuperscript{24} was used for O, while the iodine valence orbitals were described by the same basis set augmented with a pseudopotential (cc-pVQZ-pp)\textsuperscript{25} for the core orbitals (1s2s2p3s3p3d). Near the CI, the mixing angle $\alpha$ was determined and used to perform diabatization.\textsuperscript{26} The diabatization leads to a full spin-free DPEM, in which the diagonal diabatic PESs are coupled by the off-diagonal elements. Subsequently, the SO couplings are computed by using the Breit–Pauli Hamiltonian at the complete active space self-consistent field (CASSCF)\textsuperscript{27,28} level and used to further couple the spin-free states. Finally, the permutation invariant polynomial-neural network (PIP-NN) method\textsuperscript{29,30} was used in fitting for PESs and couplings.

The calculated properties are in much better agreement with experiment than the previous theory,\textsuperscript{31} thanks to the better treatment of the electron correlation. For example, equilibrium geometries and zero point energies (ZPEs) for both electronic states of O₂ listed in Table 1 are all in very good agreement with the experimental results.\textsuperscript{31} In addition, our excitation energy $(T_0)$ of O₂($a^3\Delta_g$) of 7880 cm$^{-1}$ is in excellent agreement with the experimental value of 7882 cm$^{-1}$, much better than the 8009 cm$^{-1}$ value reported by Kaledin et al.\textsuperscript{12} Our ZPE corrected exoergicity of R1 is 277 cm$^{-1}$, which is much closer to the experiment value (279 cm$^{-1}$)\textsuperscript{32} than the 406 cm$^{-1}$ value in earlier calculations.\textsuperscript{12} The calculated SO splitting for the iodine atom is 7209 cm$^{-1}$, which is close to the experimental data 7603 cm$^{-1}$\textsuperscript{33}. The discrepancy is presumably due to the more approximate theory used in such calculations. To better match the experimental SO splitting, the theoretical value was modified by multiplying a factor of 1.0546 in the PESs.

In the absence of SO coupling, the interaction of I($^3P$) with the oxygen species (O₂($X^3Σ_g^-$) and O₂($a^3\Delta_g$)) results in a collinear IOO complex in seven electronic states: $1^3Σ^−$, $1^3Π$, $1^3Σ^-$, $1^3Π$, $1^3Δ$, $2^3Π$, and $1^3Φ$. This is clearly seen in Figure 1A, involving nonadiabatic transitions are also challenging, as a quantum treatment is needed.\textsuperscript{21} Earlier theoretical models for R1 by Morokuma and co-workers have relied on a semiclassical trajectory surface hopping (TSH) treatment of nonadiabatic transitions among several relevant PESs obtained at the complete active space with the second-order perturbation theory (CASPT2) level of theory.\textsuperscript{12,13} These diabatic PESs and their couplings were expressed in two dimensions with the O–O bond length fixed at its equilibrium. While the experimental result at 150 K was reproduced, their theoretical work predicted a decay of $k_2$ with increasing temperature.\textsuperscript{15} This disagreement with experiment was attributed to an over-estimation of the attractive van der Waals interaction in the reactant channel of R1. Because of the many approximations involved in these studies, however, it is not obvious if the failure in reproducing the experimental trend is due to the inaccurate electronic structure calculations, the reduced dimensional model, or the semiclassical treatment of the dynamics. Furthermore, it is not clear which nonadiabatic coupling, SO or derivative, is dominant.

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in which the corresponding potential energy curves are plotted at the collinear geometry in the Jacobi radial coordinate \( r \) with the O–O distance \( (r) \) fixed at its ground state equilibrium (1.21 Å), and the Jacobi angle \( \gamma \) is defined as 0° for the I00 geometry. In this figure, a crossing between two states (1^2Π and 1^2Δ) is clearly visible near \( R = 2.8 \) Å, thanks to vanishing off-diagonal elements at linearity. This crossing becomes an avoided one as the molecule bends, as it develops into a symmetry-allowed CI. At the \( C_\text{str} \) geometry, these two states become four with their corresponding term symbols as \( 1^2B_1 \) and \( 1^2B_2 \) for \( 1^2Π \) and \( 1^2A_1 \) and \( 1^2A_2 \) for \( 1^2Δ \). They again cross each other in another set of symmetry-allowed CIs. These CIs are shown in Figure S1 of the Supporting Information (SI). The adiabatic PESs and derivative couplings are represented by the DPEM, in which the diagonal levels, \( I(2^{Ω}) \) on the three Jacobi coordinates. The strong SO coupling of the iodine atom leads to two SO channel states \( I(2^{Ω}) + O_2(a'Δ_p) \) channel, there are four fine-structure diabatic states labeled with \( D_{a1}, D_{a2}, D_{a3}, \) and \( D_{a4} \) corresponding to \( Ω = 3/2, 5/2, 1/2, \) and 7/2 in collinear geometry, following Kaledin et al.\textsuperscript{12,13}. The product \( I(2^{Ω}) + O_2(X^2Σ_g^-) \) channel has three fine-structure diabatic states labeled with \( D_{X1}, D_{X2}, \) and \( D_{X3} \) corresponding to \( Ω = 3/2, 1/2, \) and 1/2. Because of the mixing of the electronic states by SO coupling, the crossing in Figure 1A becomes three, as identified in the figure. The lowest crossing between the diabatic states (\( D_X \) and \( D_{a1} \)) is located at \( (R = 3.66 \) Å, \( r = 1.21 \) Å, \( γ = 50°) \) with an energy of 5344 cm\(^{-1}\), which is very close to the reactant asymptote. The SO couplings and their coordinate dependence are shown in Figure S2.

With derivative couplings, there are seven adiabatic states by labeled with \( A_{a1}, A_{a2}, A_{a3}, A_{a4}, AX_1, AX_2, \) and \( AX_3 \) corresponding to the diabatic states \( D_{a1}, D_{a2}, D_{a3}, D_{a4}, DX_1, DX_2, \) and \( DX_3 \). These adiabatic states have a relatively weak dependence on the O–O bond length \( (r) \), as shown in Figure 2A, in which PESs of the two adiabatic states (AX\(_1\) and AX\(_2\)) and \( AX_1 \) denote the product and reactant states with \( Ω = 3/2 \) and \( Ω = 5/2 \), respectively) are plotted as a function of \( R \) and \( γ \), with the angle \( γ \) fixed at 50°. This observation justifies the previous reduced-dimensional assumption of Kaledin et al.\textsuperscript{12,13}. On the other hand, the PESs are lowered as the molecule is bent, as shown in Figure 2B, where \( r \) is fixed at 1.21 Å. There are van der Waals wells in both the entrance and exit channels. As shown in Table S2, the deepest well in the reactant channel \( (Ω = 3/2) \) has a depth of 145 cm\(^{-1}\), which is shallower than 250 cm\(^{-1}\) reported by the previous work,\textsuperscript{9} suggesting less attraction.

**Table 2. Equilibrium Geometries\(^a\) and Well Depths\(^b\) in the Reactant and Product Channels**

<table>
<thead>
<tr>
<th>state</th>
<th>equilibrium geometry</th>
<th>( D_i )</th>
</tr>
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</table>
| reactant channel
| \( Ω = 7/2 \) | (4.253, 1.219, 90) | 39 |
| \( Ω = 1/2 \) | (4.079, 1.219, 90) | 115 |
| \( Ω = 5/2 \) | (4.067, 1.219, 60) | 121 |
| \( Ω = 3/2 \) | (3.972, 1.219, 90) | 145 |
| product channel
| \( Ω = 1/2 \) | (4.190, 1.210, 90) | 91 |
| \( Ω = 1/2 \) | (4.151, 1.210, 90) | 92 |
| \( Ω = 3/2 \) | (4.138, 1.210, 90) | 92 |

\(^a\) In Jacobi coordinates with the units of Å and °. \(^b\) \( D_i \) in cm\(^{-1}\).

The nuclear Hamiltonian for this system can be written as (\( \hbar = 1 \)):

\[
\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \left( \frac{(j - \sigma)}{2\mu_R R^2} \right)^2 + \frac{j^2}{2\mu_r r^2} + V(R, r, γ)
\]

(R2)

where the first two terms denote the kinetic energy operators for the radial Jacobi coordinates \( R \) (I–O, distance) and \( r \) (O–O distance).
distance), with and as the corresponding reduced masses and are the rotational angular momenta for IOO and O2, respectively, with as the Jacobi angle.

The potential (V) is best expressed in electronic bases that include electronic spin. Following our earlier work, a diabatic representation denoted as |κσ⟩ is used for deriving the DPEM. Here, and σ denote projections of the electronic and spin angular momenta onto the molecular axis of the linear IOO, respectively. For convenience, this notation is also used for bent geometries despite their lack of definition. As discussed in the SI, there are states for R1, denoted as |2s+1\ell_j; σ⟩, but only 12 are included in our model. The Kramers doublets are with labels e and f. Here, we only consider the coupling for e−e or f−f rather than e−f, because the latter is much smaller than former.

The dynamics was simulated by solving the Schrödinger equation under the Hamiltonian definition. As discussed in the SI, the centrifugal potentials (\( J(J + 1)/2\mu R^2 \)) at large J values raise the energy of the CIs to higher energies, manifesting as an effective barrier for the nonadiabatic transitions. These behaviors clearly suggest an important role of the CIs. Furthermore, the narrow features at low collision energies are attributable to resonances supported by the attractive wells in the reactant channel. On the other hand, the weak oscillations appearing in collision energies higher than 0.16 eV are due apparently to the first vibrationally excited state of O2 in the product channel, similar to what was observed in our recent work on the N2 quenching of C(2D).37

In Figure 3B, the calculated rate coefficient is compared with experimental data. The agreement with experiment is much improved over the previous theoretical results, which are also included in the figure for comparison. Most importantly, our rate coefficient has a slightly positive temperature dependence, consistent to the experimental data from Heaven’s group. The correct temperature dependence can be attributed to the emergence of an effective barrier in the nonadiabatic process, as discussed above.

As mentioned above, the reactant and product channels are coupled by both SO and derivative couplings. While the SO coupling is a necessity for the formation of the reactant and product channels as illustrated in Figure 1, the role of the derivative coupling has not been clearly understood. To throw light on the nonadiabatic mechanism, we have repeated the calculation without the off-diagonal term between the \(^1\Pi\) and \(^1\Delta\) states. The results indicate that the reaction probability (J = 0) almost vanishes (see Figure S4), suggesting an indispensable role for the derivative coupling around the CIs. An analysis of the SO Hamiltonian in the SI reveals that the SO coupling between states in the reactant channel and those in the product channel is very small, which explains the aforementioned observation. Hence, we conclude that R1 is most critically controlled by the derivative coupling near the CIs. This conclusion is consistent to the emergence of a reaction threshold and its shift with increasing J, as discussed above.

To summarize, a full-dimensional quantum dynamical study is reported for the prototypical electronic energy transfer reaction \( I(2\Sigma_g^+; \varepsilon = 0, J_0 = 1) + O_2(a^3\Delta) \rightarrow I(2\Sigma_g^+; \varepsilon + 1)/2 + O_2(a^3\Sigma_g^+; \mu = 0, J_0 = 1) \), using a newly developed accurate DPEM that includes both derivative and SO couplings. The experimental rate coefficient and its temperature dependence are well reproduced, underscoring the accuracy of the electronic structure and nonadiabatic dynamical calculations. The slightly positive temperature dependence of the rate coefficient is attributed to an emerging effective barrier for the nonadiabatic process due to the J-dependent centrifugal barrier. The CIs near the linear geometry, particularly the lowest one, play a dominant role in promoting the reaction. These new theoretical insights shed valuable light on the reaction mechanism and kinetics of this important reaction in the COIL and have important implications in other electronic energy transfer processes.
S-I. Electronic structure calculations; S-II. Fitting of PESs and couplings; S-III. Dynamical calculations; S-IV. Additional results (PDF)

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Notes
The authors declare no competing financial interest.

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