Vibrational quenching of CO₂(010) by collisions with O(³P) at thermal energies: A quantum-mechanical study

M. P. de Lara-Castells,^{a)} Marta I. Hernández, G. Delgado-Barrio, and P. Villarreal
Instituto de Matemáticas y Física Fundamental (CSIC), Serrano 123, E-28006 Madrid, Spain

M. López-Puertas
Instituto de Astrofísica de Andalucía (CSIC), Apartado 3004, E-18080 Granada, Spain

(Received 14 November 2005; accepted 2 March 2006; published online 24 April 2006)

The CO₂(010)–O(³P) vibrational energy transfer (VET) efficiency is a key input to aeronomical models of the energy budget of the upper atmospheres of Earth, Venus, and Mars. This work addresses the physical mechanisms responsible for the high efficiency of the VET process at the thermal energies existing in the terrestrial upper atmosphere (150 K ≤ *T* ≤ 550 K). We present a quantum-mechanical study of the process within a reduced-dimensionality approach. In this model, all the particles remain along a plane and the O(³P) atom collides along the C_{2v} symmetry axis of CO₂, which can present bending oscillations around the linear arrangement, while the stretching C–O coordinates are kept fixed at their equilibrium values. Two kinds of scattering calculations are performed on high-quality *ab initio* potential energy surfaces (PESs). In the first approach, the calculations are carried out separately for each one of the three PESs correlating to O(³P). In the second approach, nonadiabatic effects induced by spin-orbit couplings (SOC) are also accounted for. The results presented here provide an explanation to some of the questions raised by the experiments and aeronomical observations. At thermal energies, nonadiabatic transitions induced by SOC play a key role in causing large VET efficiencies, the process being highly sensitive to the initial fine-structure level of oxygen. At higher energies, the two above-mentioned approaches tend to coincide towards an impulsive Landau-Teller mechanism of the vibrational to translational (V-T) energy transfer. © 2006 American Institute of Physics. [DOI: 10.1063/1.2189860]

I. INTRODUCTION

The population of the CO₂(010) level (the bending mode) in the upper atmosphere of the terrestrial planets (Earth, Mars, and Venus) is an essential input to aeronomical models. This level is the main source of the 15 μm emission that produces the largest cooling process in the upper mesosphere and lower thermosphere, and thus has a dominant impact on the kinetic temperatures and density structure. Thermal collisions with atomic oxygen, CO₂(000)+O(³P) → CO₂(010)+O(³P), constitute the major mechanism controlling the vibrational population of CO₂(010). The latter vibrational energy transfer (VET) process plays, in fact, such a dominant role that the corresponding rate constant is considered the most important parameter in analyzing the measurements of the CO₂ 15 μm atmospheric radiance.¹

Numerous experimental, field and laboratory, measurements of the rate constant *k* for the quenching process CO₂(010)+O(³P) → CO₂(000)+O(³P) have been performed (this relaxation rate is more straightforward to measure and is related to the up-pumping rate through the principle of a detailed balance). In spite of this intense study, a 50% uncertainty in *k* is assumed in modeling the 15 μm emission from planetary thermospheres.² In addition, the temperature dependence of *k* is not well known in the atmospheric temperature range (150–550 K). Taylor,³ based on high-temperature

(1975–3840 K) shock-tube measurements by Center,⁴ reported an expression for *k*(*T*) with a Landau-Teller temperature dependence, *A* exp(−*BT*^{−3}), which gives a room-temperature value of 2.4 × 10^{−14} cm³ s^{−1}. On the other hand, using field-based data of atmospheric 15 μm radiance, Sharma and Wintersteiner⁵ recommended a value of 6(±3) × 10^{−12} cm³ s^{−1} of *k* at 300 K, i.e., a factor of about 250 larger than Taylor's extrapolation. In order to account for this discrepancy, they proposed an expression for *k*(*T*) in which a low-temperature, *CT*^{1/2}, term is added to the Landau-Teller term. During the last decade, laboratory determinations of the relaxation rate have been reported at room temperature,^{6–9} providing values in the (1–1.5) × 10^{−12} cm³ s^{−1} range. Nevertheless, the value of *k* required by the atmospheric models is about a factor of 4 larger than the measured values.^{1,10} More recently, Castle *et al.*,¹¹ using the temperature-jump method, have obtained a larger value of the vibrational relaxation rate coefficient, placing it below the low end of the range of aeronomical estimates.

In spite of its importance, there are no quantum-mechanical studies based on accurate *ab initio* PESs addressing the quenching of CO₂(010) by O(³P) at atmospheric temperatures. The most recent theoretical study for this process was carried out by Scott *et al.*,¹² assuming a perpendicular approach of the colliding particle and performing quasi-classical trajectory calculations on an adjustable Morse-type CO₂–O interaction potential. This single-surface approach was capable of describing the high-temperature dependence

^{a)}Electronic mail: delara@imaff.cfmac.csic.es

FIG. 1. OCO angle bisector body-frame coordinate system employed for the PES calculations of the CO₂+O collisional system.

of k . To reproduce the low-temperature dependence of the relaxation rate constant, however, Scott *et al.* resorted to a curve-crossing model proposed by Nikitin and Umanski¹³ for VET processes involving open-shell species. Earlier investigations, using either trajectories¹⁴ or close-coupling¹⁵ treatments, focused on the calculation of the quenching of CO₂ by oxygen colliding at relatively high kinetic energies (above 1 eV). These studies were based entirely on repulsive potentials fitted to a few *ab initio* points.¹⁶ Additional electronic structure calculations (e.g., see Refs. 17–19) on the triplet CO₂–O system addressed mainly the molecular properties of the strongly bound CO₃ isomers existing in the regions of the potential energy surfaces (PESs) related to the O(¹D)+CO₂ reaction. These regions, due to the existence of very high-energy (above 1.5 eV) transition barriers, can only be reached with hyperthermal O(³P) atoms.¹⁸ However, the van der Waals (vdW) regions of the PESs, which are the relevant ones in collisions of CO₂ with O(³P) at thermal energies, have not been investigated yet.

As a first attempt to characterize, on a full quantum-mechanical level, the physical mechanisms involved in CO₂(010)+O(³P) collisions at thermal energies, we have performed quantum scattering calculations on high-level *ab initio* PESs of the three electronic states correlating with the O(³P)+CO₂ (¹Σ_g⁺) asymptote. A reduced-dimensionality approach has been adopted in which only the two most significant degrees of freedom are included. We assume that the oxygen atom approaches the CO₂ molecule in the plane of CO₂ in a C_{2v} geometry (which corresponds to the global vdW minimum). The C–O distances in CO₂ are fixed to their equilibrium values, leaving the two active coordinates as the intermolecular distance between the oxygen atom and the CO₂ center of mass, and the intramolecular CO₂ bending angle. Scattering calculations are performed first on each of the different electronic states to test the importance of a pure V-T energy transfer mechanism.

The non-Landau-Teller behavior of k at low temperatures suggests that the mechanism of energy transfer may also involve vibrational to electronic (V-E) transitions. As pointed out by Sharma and Roble,¹ since the atomic fine-

structure splitting of the O(³P_{*j*}) levels [$E(^3P_2 - ^3P_1) = 158.265$ cm⁻¹, $E(^3P_2 - ^3P_0) = 226.977$ cm⁻¹] (Ref. 20) is comparable to both the energy difference (667 cm⁻¹) between the (000) and (010) vibrational states of CO₂ and the energy separation between the different electronic states in the vdW region, spin-orbit couplings (SOCs) may have an important effect in relaxing the (010) bending level of CO₂. Therefore, we also consider spin-orbit induced intersystem crossing effects, and, in a second approach, the multiplets and nonadiabatic transitions induced by SOCs are accounted for. A comparison with the pure V-T scattering calculations allows an assessment of the importance of spin-orbit interactions in the VET mechanism.

In the following section, we describe the electronic structure calculations. In Sec. III, the Hamiltonian model and the method to solve the scattering problem are described. The results on vibrational quenching probabilities are presented and discussed in Sec. IV. Finally, we conclude with a summary of the main results and some plans for future work.

II. ELECTRONIC STRUCTURE

A. Interaction energies

The interaction energies of the complex were evaluated at the spin-restricted single and double coupled-cluster level with a perturbative treatment of triple excitations [RCCSD(T)] as implemented in MOLPRO 2002²¹ at the frozen core approximation. The augmented correlation-consistent polarized triple zeta (aug-cc-pVTZ) atomic basis set²² supplemented by a (3s3p2d2f1g) set of midbond functions^{23,24} was used throughout the calculations. The basis set superposition error (BSSE) was corrected using the full-counterpoise scheme of Boys and Bernardi²⁵ and Jansen and Ros.²⁶ Therefore, the interaction energy at each geometry was calculated as

$$U_{\Gamma}^{\text{int}}(R, \theta, \alpha) = E_{\Gamma}^{\text{CO}_2-\text{O}}(R, \theta, \alpha) - [E^{\text{CO}_2}(R, \theta, \alpha) - E_{\Gamma}^{\text{O}}(R, \theta, \alpha)], \quad (1)$$

where Γ stands for the spatial symmetry of the electronic

state and E^{CO_2} , E_{Γ}^{O} , and $E_{\Gamma}^{\text{CO}_2-\text{O}}$ are the electronic energies of CO₂, O, and CO₂-O, respectively, calculated in the complete CO₂-O basis set. Since the presence of ghost orbitals breaks the symmetry of the O atom, we used separate monomer *counterpoise* states for separate Γ -symmetry electronic states of the dimer. As seen in Fig. 1, the coordinates R , θ , and α represent the distance from the O atom to the center of mass of CO₂, the angle formed by the vector $\mathbf{R}$ connecting the centers of mass and the C_{2v} symmetry axis of CO₂, fixed to zero in the present calculations, and the intramolecular bending angle, respectively. The C-O internuclear distances of CO₂ were fixed at their optimized RCCSD(T)/aug-cc-pVTZ equilibrium value, $r_e=1.167$ Å, which has a relative error of 0.4%, compared to the experiment.²⁷ We have verified, by using the larger aug-cc-pVQZ and aug-cc-pV5Z basis sets, that the interaction energies near the minimum are converged to within 1 cm⁻¹. Also, the value of the T_1 diagnostic,²⁸ surpassing the threshold of 0.020 for the relevant range of intermolecular distances, confirms that the single reference coupled-cluster approach is adequate. We used an R grid of 36 points ranging from 1.8 to 15 Å and an α grid of 13 points between $\alpha=150^\circ$ and 210° in steps of 10° . All calculated interaction energies are available upon request.

The collision between O(³P) atoms and the ground state CO₂ (¹ Σ_g^+) involves three electronic surfaces that correlate to O(³P). In Fig. 2 the interaction potentials of the three electronic states CO₂-O in the C_{2v} geometry are represented for selected values of the CO₂ bending angle. We discuss first the potential energy curves (PECs) with the bending angle fixed at the CO₂ equilibrium ($\alpha=180^\circ$, solid lines). The minimum occurs in an ³A₂ spatial symmetry state at $R=3.1$ Å with a related well depth of 335.5 cm⁻¹. For this geometry, a local minimum is found in the ³B₁ state ($R=3.1$ Å, $D_e=106.7$ cm⁻¹), whereas the ³B₂ state is repulsive. The assignment of the four 2*p* electrons of the oxygen atom in the A₂, B₁, and B₂ states are $p_x^1 p_y^1 p_z^2$, $p_x^1 p_y^2 p_z^1$, and $p_x^2 p_y^1 p_z^1$, respectively. In the A₂ state, the p_z orbital, pointing toward the positively polarized C in CO₂, is doubly occupied, giving rise to a more favorable concerted quadrupole-quadrupole and induced dipole-quadrupole interactions than those in the B₁ and B₂ orbital arrangements. On the contrary, the double occupation of the p_x orbital in the B₂ state is expected to result in a stronger Pauli exchange repulsion from the p lone pairs at the terminal O atoms of CO₂. This results in a repulsive state. In the B₁ state, the doubly occupied orbitals are orthogonal to the CO₂ plane, so the exchange repulsion is weaker than that in the B₁ and A₂ states. The splitting of the three states is already clear at the restricted Hartree-Fock (RHF) level. Thus, the RHF T-shape PEC has a minimum in the A₂ state ($R=3.4$ Å, $D_e=125.1$ cm⁻¹), whereas the RHF calculations of the B₁ and B₂ states reveal purely repulsive PECs.

The dependence with the α bending angle is also shown in Fig. 2. For $\alpha < 180^\circ$ ($> 180^\circ$) the CO₂ molecule bends toward (away from) the colliding oxygen atom (see Fig. 1). Note that the PECs for the two different directions of scissoring are not symmetric. The degree of symmetry breaking is related directly to the magnitude of the vibrational cou-

FIG. 2. Interaction potentials of the ³A₂, (bottom panel), ³B₁ (middle panel), and ³B₂ (upper panel) electronic states of CO₂-O for selected values of the bending coordinate of CO₂. Solid lines: $\alpha=180^\circ$. Dashed lines: $\alpha=150^\circ$. Dotted lines: $\alpha=210^\circ$.

pling between the (000) and (010) states of CO₂ due to the interaction with oxygen. We will comment further on this point below. Note, too, that the three PECs behave differently depending on the direction of bending. For the ³A₂ state, the bending of CO₂ away from the oxygen atom makes the well depth deeper than that with CO₂ at equilibrium. For both ³B₂ and ³B₂ states, the bending of CO₂ toward the colliding particle gives rise to a stronger attractive interaction. Thus, the ³B₂ state, which is repulsive with the CO₂ at equilibrium, becomes attractive at $\alpha=150^\circ$. These features can be understood by considering, for the different states, the induced moment adopted by oxygen to optimize the interaction. In fact, the value of the induced dipole moment along the z axis^{29,30} for the oxygen atom in the ³A₂ state is about -0.97 a.u. to be compared with values of about 0.48 a.u. in the ³B₁ and ³B₂ states. In addition, depending on the direction of bending, the sign of the dipole moment of the CO₂ molecule is positive ($\alpha < 180^\circ$) or negative ($\alpha > 180^\circ$). Therefore, in the A₂ state for $\alpha > 180^\circ$, the sign of the dipole moments adopted by both CO₂ and O monomers is negative, resulting in an attractive dipole-induced dipole interaction, which increases the well depth. Conversely, in the ³B₁ and ³B₂ states, for $\alpha > 180^\circ$, the signs of the monomer dipoles are opposite, giving rise to a repulsive dipole-induced dipole interaction which raises the potential energy curve over that for CO₂ at equilibrium ($\alpha=180^\circ$).

TABLE I. States coupled within each Γ_i block of the full-effective ($\hat{H}_{\text{el}} + \hat{H}_{\text{so}}$) Hamiltonian matrix. The $O(^3P_j)$ fine-structure states that are obtained by diagonalizing the Hamiltonian at $R \rightarrow \infty$ within each Γ_i block are also shown, along with their degeneracy.

Γ_i	A_1	B_1	B_2	A_2
	$A_2\Theta_z$ $B_1\Theta_y$ $B_2\Theta_x$	$A_2\Theta_x$ $B_2\Theta_z$	$A_2\Theta_y$ $B_1\Theta_z$	$B_1\Theta_x$ $B_2\Theta_y$
Number of j states at $R \rightarrow \infty$				
$j=0$	1	...	...	...
$j=1$	...	1	1	1
$j=2$	2	1	1	1

A comparison with results on the $\text{CO}_2\text{-Ne}$ complex³¹ and other $\text{CO}_2\text{-rare-gas}$ atom complexes (see, for example, Ref. 32) indicates that the global minimum is in a T-shape geometry. However, the well depths are over a factor of 3 larger in $\text{CO}_2\text{-O}$ (335.5 vs 84.61 cm^{-1}) than in $\text{CO}_2\text{-Ne}$. This difference is observed even at the RHF level, so the $\text{CO}_2\text{-O}$ complex is bound at the RHF level, whereas the RHF $\text{CO}_2\text{-Ne}$ interaction potential is purely repulsive. Unlike the Ne atom, the O atom has a permanent quadrupole, which causes the electrostatic interaction to play an important role for the $\text{CO}_2\text{-O}$ complex. On the contrary, the $\text{CO}_2\text{-Ne}$ complex is stabilized mainly by dispersion energy, which is a pure correlation effect.

We have also considered additional geometries for the complex and found that the interaction energies are significantly higher than those at the T-shaped geometry in the vdW region. The results of these electronic structure calculations will be reported separately.³³

B. Spin-orbit couplings

The SOC matrix elements have been calculated using the full Breit-Pauli Hamiltonian following the scheme of Berning *et al.*,³⁴ as implemented within MOLPRO. We used an uncontracted cc-pVTZ basis set and an active-space self-consistent field (CASSCF) treatment with a restricted active space in which the 1s and 2s orbitals were fixed to double occupancy. The asymptotically degenerate $^3A_2$, $^3B_1$, and $^3B_2$ states were state averaged to produce equivalent p_x , p_y , and p_z orbitals in the dissociation limit. For the separated O atom with the present ansatz [no second-order spin-orbit effects arising from the coupling with the $O(^1D)$ and $O(^1S)$ states were considered], the fine-structure levels of $O(^3P_j)$ are calculated to be 0.0 (0.0, $j=2$), 156.56 (158.265, $j=1$), and 234.84 (226.977, $j=0$) in cm^{-1} (experimental values in parentheses²⁰).

As found in previous investigations of the $\text{O}_2\text{-O}(^3P)$ and $\text{SO-O}(^3P)$ systems by Rosmus and co-workers,^{35,36} the main contribution to the SOC in the vdW region is derived from the atomic term $O(^3P)$. Thus, for $R \geq 2.4$ Å the deviation of the matrix elements from the asymptotic value amounts to less than 0.5 cm^{-1} , implying that oxygen largely behaves as an isolated atom. This is in contrast to the interaction energies which do not approach their asymptotic lim-

its up to $R \geq 5.0$ Å. This can be roughly explained by comparing the interparticle distance dependence of the spin-orbit (r^{-3}) and electrostatic Hamiltonian (r^{-1}) operators, the former being more short ranged. As a consequence, the R and α dependences of the coupling matrix elements are extremely weak, and we have ignored it in the present study.

The full effective electronic Hamiltonian matrix is represented in the basis of the electronic nonrelativistic wave functions, denoted as $\xi_\Gamma(\{q_i^{\text{el}}\}; R, \alpha)$ ($\{q_i^{\text{el}}\}$ are the electronic coordinates), multiplied by symmetry-adapted spin functions that transform as irreducible representations of rotation:

$$\Theta_z[A_2] = \Theta_{M_s=0},$$

$$\Theta_x[B_2] = -\frac{1}{\sqrt{2}}(\Theta_{M_s=1} - \Theta_{M_s=-1}), \quad (2)$$

$$\Theta_y[B_1] = \frac{i}{\sqrt{2}}(\Theta_{M_s=1} + \Theta_{M_s=-1}),$$

where the associated symmetry is indicated in brackets. In this basis, the spin-orbit Hamiltonian matrix elements are real. The selection rules of the spin-orbit matrix are given in the Appendix. The resulting products of the wave functions are grouped together according to symmetry to form appropriate matrices for each of the four C_{2v} group representations. This leads to a factorization of the 9×9 Hamiltonian matrix into one 3×3 (A_1 symmetry) and three 2×2 (B_1 , B_2 , and A_2) blocks. Table I displays the different states (Γ_i, Θ_μ) coupled within each global symmetry block, hereafter denoted as Γ_i . Diagonalization of this full effective Hamiltonian matrix in the asymptotic limit yields fivefold ($j=2$), threefold ($j=1$), and onefold ($j=0$) degenerate fine-structure states of the O atom. In particular, the diagonalization of the A_1 sub-block gives rise to two degenerate $O(^3P_2)$ and one $O(^3P_0)$ atomic fine-structure levels, whereas diagonalizing the remaining 2×2 sub-blocks produces one $O(^3P_1)$ level and one $O(^3P_2)$ level.

III. THE THEORETICAL MODEL

A. Hamiltonian

As mentioned previously, we use a coplanar model in which the oxygen atom collides with CO_2 in a C_{2v} approach ($\theta=0$ in Fig. 1), and the stretching C–O degrees of freedom are frozen to their equilibrium distances. This model was chosen because the largest vibrational couplings between the (000) and (010) states of CO_2 are expected to occur for the perpendicular direction of collision. Note, too, that for the linear geometry ($\theta=90^\circ$) the intermolecular potential is symmetric around $\alpha=180^\circ$, and thus the associated couplings are strictly zero there. In addition, preliminary calculations at $\theta=45^\circ$ indicate that the absolute values of the vibrational couplings in the minimum vdW region are more than two times smaller than those at the T-shape configuration.³³ Therefore, these geometries are expected to be less important for scattering at thermal energies.

The dynamics thus involves two primary active degrees of freedom, the intermolecular distance R and the CO_2 bend-

ing angle α for three adiabatic PESs, which are further coupled by spin-orbit interactions. The total Hamiltonian can be written as³⁷

$$\hat{H} = -\frac{\hbar^2}{2\mu_{\text{O-CO}_2}} \left[\frac{\partial^2}{\partial R^2} + \frac{1}{4R^2} \right] + \hat{T}_{\text{CO}_2} + \hat{H}_{\text{el}}(\{q_i^{\text{el}}\}; R, \alpha) + \hat{H}_{\text{so}}(\{q_i^{\text{el}}\}; R, \alpha), \quad (3)$$

where the first term corresponds to the nuclear kinetic energy operator associated with the scattering coordinate R and $\mu_{\text{O-CO}_2} = m_{\text{O}}(m_{\text{C}} + 2m_{\text{O}})/(m_{\text{C}} + 3m_{\text{O}})$ is the reduced mass. The second term is the nuclear kinetic energy term of the isolated CO₂ partner, which depends on the bending angle α ,

$$\hat{T}_{\text{CO}_2} = -\frac{\hbar^2}{r_e^2} \left\{ \left(\frac{1}{\mu_{\text{oc}}} - \frac{\cos \alpha}{m_{\text{c}}} \right) \frac{\partial^2}{\partial \alpha^2} + \frac{\sin \alpha}{m_{\text{c}}} \frac{\partial}{\partial \alpha} + \frac{1}{4} \left(\frac{1}{\mu_{\text{oc}}} + \frac{\cos \alpha}{m_{\text{c}}} \right) \right\}. \quad (4)$$

Finally, the third and fourth terms of Eq. (3), $\hat{H}_{\text{el}}$ and $\hat{H}_{\text{so}}$, are the electronic (nonrelativistic) and spin-orbit (Breit-Pauli) Hamiltonians, respectively, depending on the electronic coordinates $\{q_i^{\text{el}}\}$ as well as, parametrically, on R and α . In our basis $[\xi_{\Gamma}(\{q_i^{\text{el}}\}; R, \alpha) \Theta_{\mu}]$ the full electronic Hamiltonian ($\hat{H}_{\text{el}} + \hat{H}_{\text{so}}$) matrix elements within each Γ_i global symmetry block are given by

$$H_{\Gamma_{\Theta_{\mu'} \Gamma' \Theta_{\mu}}}^{(\Gamma_i)} = U_{\Gamma}(R, \alpha) \delta_{\Gamma \Gamma'} \delta_{\Theta_{\mu'} \Theta_{\mu}} + H_{\Gamma_{\Theta_{\mu'} \Gamma' \Theta_{\mu}}}^{\text{so}} (1 - \delta_{\Gamma \Gamma'}) \times (1 - \delta_{\Theta_{\mu'} \Theta_{\mu}}), \quad (5)$$

where $U_{\Gamma}(R, \alpha) = \langle \xi_{\Gamma} | \hat{H}_{\text{el}} | \xi_{\Gamma} \rangle_{\{q_i^{\text{el}}\}}$ is the PES of electronic state Γ (which does not depend on M_s and therefore on the particular spin function in Eq. (2)). At $R \rightarrow \infty$, U_{Γ} correlates with the energy of the oxygen atom plus the CO₂ potential energy, $U_{\text{CO}_2}(\alpha)$, in the $^1\Sigma_g^+$ electronic state in which the two O-C bond distances have been frozen. Hence $U_{\Gamma}(R, \alpha) = U_{\Gamma}^{\text{int}}(R, \alpha) + U_{\text{CO}_2}(\alpha)$. The term $H_{\Gamma_{\Theta_{\mu'} \Gamma' \Theta_{\mu}}}^{\text{so}}$ in Eq. (5) represents the asymptotic, $R \rightarrow \infty$, spin-orbit coupling matrix elements. As mentioned above, due to the weak α and R dependences of the couplings, they can be safely fixed to their asymptotic values.

B. Inelastic scattering formulation

To perform the scattering calculations, we use the R -matrix propagation method of Light and co-workers.^{38,39} This method determines the solution of the Schrödinger equation for the scattering wave function $\Phi_{n'}$, $\hat{H} \Phi_{n'} = E_{\text{tot}} \Phi_{n'}$, where the Hamiltonian is given by Eq. (3), E_{tot} is the total energy, and n' labels the initial state. In this method, the scattering coordinate R is divided into N_{sect} equidistant sectors R_j , where R_j denotes the midpoint of each sector. In every sector the total wave function $\Phi_{n'}$ is expanded in a close-coupling form,

$$\Phi_{n'}(R, \alpha, \{q_i^{\text{el}}\}; R_j) = \sum_{n=1}^N g_{n,n'}(R; R_j) \phi_n(\alpha, \{q_i^{\text{el}}\}; R_j),$$

where N denotes the total number of channels included in the expansion and ϕ_n are eigenfunctions of the so-called surface Hamiltonian $\hat{H}_S$ which depends on R parametrically and is therefore the *frozen* R part of the total Hamiltonian:

$$\hat{H}_S(\alpha, \{q_i^{\text{el}}\}; R_j) = -\frac{\hbar^2}{8\mu_{\text{O-CO}_2} R_j^2} + \hat{T}_{\text{CO}_2}(\alpha) + \hat{H}_{\text{el}}(\{q_i^{\text{el}}\}; R_j, \alpha) + \hat{H}_{\text{so}}(\{q_i^{\text{el}}\}; R_j, \alpha). \quad (6)$$

Starting from a small value of R in the classically forbidden region, the wave functions $g_{n,n'}(R; R_j)$ are propagated from one sector to the next out to large R by means of the R -matrix propagation method, which involves the calculation of the overlap matrix between the surface eigenfunctions corresponding to two adjacent sectors, j and $j+1$, $\mathcal{O}_{n,n'}(j, j+1) = \langle \phi_n(\alpha, \{q_i^{\text{el}}\}; R_j) | \phi_{n'}(\alpha, \{q_i^{\text{el}}\}; R_{j+1}) \rangle$. In the asymptotic region, boundary conditions are imposed to obtain the S matrix (and hence the state-to-state probabilities):

$$g_{n,n'}(R; R_j) \xrightarrow{R_j \rightarrow \infty} \delta_{nn'} \frac{\exp[-i\lambda_n R]}{\sqrt{\lambda_n}} - S_{n,n'} \frac{\exp[i\lambda_n R]}{\sqrt{\lambda_n}},$$

with $\lambda_n^2 = 2\mu_{\text{O-CO}_2} [E_{\text{tot}} - \mathcal{E}_n(\infty)]/\hbar^2$, where $\mathcal{E}_n(\infty)$ are the eigenvalues of the surface Hamiltonian for $R \rightarrow \infty$, also called surface energies or adiabats.

To solve the surface equation $(\hat{H}_S - \mathcal{E}_n) \phi_n = 0$, the wave functions ϕ_n are expanded as

$$\phi_n(\alpha, \{q_i^{\text{el}}\}; R_j) = \sum_{v, \Gamma_{\Theta_{\mu}}} c_{v, \Gamma_{\Theta_{\mu}}}^n(R_j) \chi_v(\alpha) \xi_{\Gamma}(\{q_i^{\text{el}}\}; R_j, \alpha) \Theta_{\mu}, \quad (7)$$

where $\{\chi_v\}$ are the basis functions describing the vibrations of the isolated CO₂. As usual, they are obtained by solving variationally the time-independent Schrödinger equation associated with the Hamiltonian $(\hat{T}_{\text{CO}_2} + U_{\text{CO}_2} - \epsilon_v) \chi_v = 0$. To this end, the potential $U_{\text{CO}_2}(\alpha)$ is expanded in a series of $\cos((2m+1)\alpha/2)$ (from $m=0$) to account for its symmetry about 180°, while the χ_v functions are expanded in terms of $\sin(k\alpha/2)$ (from $k=1$). With these choices, all the necessary matrix elements are analytical.³⁷ Furthermore, the vibrational matrix elements

$$V_{vv'}^{\Gamma}(R) = \langle \chi_v | U_{\Gamma}^{\text{int}} + \hat{T}_{\text{CO}_2} + U_{\text{CO}_2} - \frac{\hbar^2}{8\mu_{\text{O-CO}_2} R^2} | \chi_{v'} \rangle_{\alpha} = \langle \chi_v | U_{\Gamma}^{\text{int}} | \chi_{v'} \rangle_{\alpha} + \left(\epsilon_v - \frac{\hbar^2}{8\mu_{\text{O-CO}_2} R^2} \right) \delta_{vv'}, \quad (8)$$

are easily obtained after the expansion,³⁷ at each R value, of U_{Γ}^{int} in terms of Legendre polynomials $P_{\lambda}(\cos(\alpha))$. The surface Hamiltonian matrix elements are given explicitly by

FIG. 3. Vibrational matrix elements $V_{vv'}^{\Gamma}(R)$ [Eq. (8)] as functions of the intermolecular distance. (a) Diagonal elements for $v=0, 1$; (b) off-diagonal couplings V_{01} . Energies are in cm^{-1} and distance in angstrom.

$$\begin{aligned}
 H_{\Gamma\Theta_{\mu}^v, \Gamma'\Theta_{\mu'}^{v'}}^{S(\Gamma)}(R_j) &= V_{vv}^{\Gamma}(R_j) \delta_{\Gamma\Gamma'} \delta_{\Theta_{\mu}\Theta_{\mu'}} \delta_{vv'} + V_{vv'}^{\Gamma}(R_j) \delta_{\Gamma\Gamma'} \delta_{\Theta_{\mu}\Theta_{\mu'}} (1 - \delta_{vv'}) \\
 &+ H_{\Gamma\Theta_{\mu}^v, \Gamma'\Theta_{\mu'}^{v'}}^{\text{so}} (1 - \delta_{\Gamma\Gamma'}) (1 - \delta_{\Theta_{\mu}\Theta_{\mu'}}) \delta_{vv'}. \quad (9)
 \end{aligned}$$

IV. SCATTERING CALCULATIONS

A. Surface states

To produce the surface states, we begin by calculating the vibrational levels of the isolated CO_2 as described in Sec. III. We obtain a (000)-(010) transition frequency of 666.2 cm^{-1} , in good agreement with the experimental value of 667 cm^{-1} (Ref. 27). For $v=0$ and $v=1$, the diagonal and off-diagonal vibrational matrix elements $V_{vv'}^{\Gamma}$, are depicted in Fig. 3 for the three spatial symmetry states. Note in Fig. 3(a) that the shapes of the diagonal terms are very similar to the PECs at $\alpha=180^\circ$ in Fig. 2. Figure 3(b) shows that the off-diagonal matrix elements have, in general, rather small values. Indeed, absolute values of these couplings become larger than the SOC constant ($\sim 77 \text{ cm}^{-1}$) just for quite small intermolecular distances. On the other hand, note that the $^3B_1$ and $^3B_2$ vibrational couplings are almost identical and have opposite signs to the $^3A_2$ one. This is a consequence of the different behavior of the CO_2+O interaction with the bending angle for the three spatial symmetry states (see Sec. II).

Surface states of Eq. (7) were computed for a grid of 600 sectors in R (from 1.8 to 15.0 Å) using a basis of five CO_2 vibrational states (from $v=0$ to $v=4$), including both vibrational and SOC for the four global symmetries specified in Table I. The surface eigenenergies as functions of the sector values (adiabats) are displayed in Fig. 4, corresponding to

FIG. 4. Eigenenergies (in cm^{-1}) of the surface Hamiltonian of Eq. (6) (adiabats) as functions of the intermolecular distance (in angstrom), $\mathcal{E}_n(R)$, for the global symmetry block A_1 . Correlation to fragment states $\text{CO}_2(0v0) + \text{O}(^3P_j)$ is indicated.

the A_1 block. For this global symmetry, each pair of states of the three spatial symmetries A_2 , B_1 , and B_2 is coupled by a constant value of about 77 cm^{-1} . Adiabats correlate asymptotically to $\text{CO}_2(0v0) + \text{O}(^3P_j)$ with $j=0, 2$ (note that the $j=2$ is twofold degenerate). In this region, the three nonrelativistic electronic wave functions are well mixed in the corresponding surface wave functions ϕ_n . Near the vdW minima (around 3 Å), however, the three lowest surface states can be well assigned (with weights of about 90%) each to the $^3A_2$, $^3B_1$, and $^3B_2$ states and the same follows for the subsequent triplets associated with each CO_2 vibrational state. This is because the vdW interaction has already split the energies of the $^3A_2$, $^3B_1$, $^3B_2$ states, so SOC works in this region as a weaker perturbation. Spin-orbit interactions become again qualitatively important for shorter intermolecular distances. Thus, when SOC are neglected there are crossings between states belonging to different spatial symmetries [see Fig. 3(a)] which become avoided crossings once SOC are included, as can be noticed in Fig. 4. We will discuss below the consequences of this behavior.

In order to assess the effect of SOC, calculations were also performed in the absence of such couplings, that is, just including vibrational couplings within each spatial symmetry. In contrast to Fig. 4, the resulting adiabats are almost identical to the diagonal matrix elements shown in Fig. 3(a). This behavior is due to the small values of the vibrational couplings for intermolecular distances larger than 2.5 Å and anticipates that spin-orbit interactions will play a key role in the dynamics.

B. Vibrational relaxation probabilities

State-to-state probabilities were computed for every global symmetry block of Table I. In the asymptotic region, surface states n were assigned to vibrational v (CO_2) and atomic angular momentum j quantum numbers. Note that for the A_1 symmetry there are two states correlating to $j=2$. Therefore, we have added a further label k which runs from one to $k_{\text{max}}(\Gamma, j)$, the degeneracy of a j state within a given Γ block (indicated in the lower part of Table I), so that the

FIG. 5. Probabilities (in log scale) of CO₂(010) quenching by atomic oxygen as functions of the total energy (in cm⁻¹). (a) Neglecting spin-orbit couplings, CO₂(010)+O(³P)→CO₂(000)+O(³P), for the different spatial symmetry states (³A₂, ³B₁, and ³B₂). (b) Including spin-orbit couplings for the different initial atomic angular momenta *j*, CO₂(010)+O(³P_{*j*})→CO₂(000)+O(³P_{*j'*}) (probabilities are summed over all final *j'* states and their multiplets). The zero of energy corresponds to the CO₂(000)+O(³P) asymptotic limit. A detailed view of the *j*=2 probability (in normal scale) as a function of the kinetic energy (corresponding to a range of translational temperatures up to about 700 K) is shown in the inset. See text for discussion.

complete asymptotical assignment is $n \equiv (v, j, k)$. We have focused on the quenching probability of CO₂(010) by oxygen in selected initial atomic angular momentum states, $P_{1j \rightarrow 0}$. To obtain this quantity, it is necessary to consider all the Γ_t blocks in which the selected *j* state is involved, as well as to average over the initial $2j+1$ multiplet and sum over all final *j'* states and their multiplets. The desired probability may be written as

$$P_{1j \rightarrow 0} = \frac{1}{2j+1} \sum_{\Gamma_t \ni j} \sum_{k=1}^{k_{\max}(\Gamma_t, j)} \sum_{j' \in \Gamma_t} \sum_{k'=1}^{k_{\max}(\Gamma_t, j')} P_{(1jk) \rightarrow (0j'k')},$$

where $[\Gamma_t \ni j]$ indicates a sum over all blocks in which the asymptotic *j* state is defined, $[j' \in \Gamma_t]$ is a sum over all *j'* states defined in a given Γ_t block, and $P_{(1jk) \rightarrow (0j'k')}$ are the state-to-state probabilities.

As mentioned above, vibrational quenching probabilities were also computed in the absence of SOCs. The $P_{1 \rightarrow 0}^{3A_2}$, $P_{1 \rightarrow 0}^{3B_1}$, and $P_{1 \rightarrow 0}^{3B_2}$ probabilities are reported in Fig. 5(a). As

expected the single-surface calculations produce very small values of the relaxation probabilities, particularly in the lower energy range and for the ³A₂ PES. Interestingly, the energy dependence of the probabilities for the three different PESs can be roughly mapped onto the *R* dependence of the V_{01} vibrational couplings (see Fig. 3(b)). The idea behind this qualitative matching is that vibrational couplings are effective in the range of intermolecular distances near the classical turning point of the diagonal term V_{11} , at a given collision energy. Thus, for large intermolecular distances $V_{01}^{3A_2}$ is larger than the couplings for the ³B₁ and ³B₂ states. This explains why $P_{1 \rightarrow 0}^{3A_2}$ is the largest at low collision energies. On the contrary, as the intermolecular distance decreases, the absolute values of $V_{01}^{3B_1}$ and $V_{01}^{3B_2}$ increasingly overcome the ³A₂ coupling. As a result, relaxation probabilities associated to those states rise above the ³A₂ probability for energies greater than 2000 cm⁻¹. In fact, as a consequence of the very small value of $V_{01}^{3A_2}$ at $R \sim 2.2$ Å, $P_{1 \rightarrow 0}^{3A_2}$ decays to almost zero for collision energies around 4500 cm⁻¹.

Vibrational relaxation probabilities for the different fine-structure states of the colliding particle are shown in Fig. 5(b). Whereas for *j*=0 and 1 the probabilities resemble the $P_{1 \rightarrow 0}^{3B_1}$ and $P_{1 \rightarrow 0}^{3B_2}$ ones of Fig. 5(a), the *j*=2 probability exhibits a qualitatively different behavior: it is much higher at low collision energies and increases with energy in a smoother fashion. This can be understood from the analysis of the states and energies of the surface Hamiltonian. In the case of the A₁ global symmetry, which gives the highest quenching probabilities in the lower energy range, three states (*n*=4, 5, and 6) correlate to fragments with vibrationally excited CO₂, the *n*=4 and 5 ones corresponding to atomic angular momentum *j*=2 and the *n*=6 one to *j*=0. As can be seen in Fig. 4, the states asymptotically assigned to *j*=2 undergo avoided crossings with the *n*=3 state, which correlates asymptotically to the ground state CO₂. However, no such avoided crossings with states correlating to CO₂(000) are found when the initial state is *n*=6, since that curve is much more repulsive. This is the origin of the enhanced vibrational quenching for the initial atomic angular momentum *j*=2 in comparison with the initial *j*=0. A similar situation occurs for the other symmetry blocks, which involve fragments with *j*=1 and 2, and where avoided crossings with states correlating with vibrationally relaxed CO₂ only occur for states correlating with CO₂(010) and *j*=2. This type of mechanism was early proposed by Nikitin and Umansky¹³ for collisions involving open-shell atoms or molecules and later postulated by Scott *et al.*¹² to explain the large value of the relaxation rate of CO₂(010)+O observed at room temperature. Moreover, we have found that, for the initial state *j*=2 and low collision energies, the largest populations are obtained for products with *j*=0 and 1. This is consistent with the proposed mechanism since the states in the CO₂(000) manifold which undergo avoided crossings with upper states are precisely those with the asymptotical labeling *j*=0 or 1 [in the A₁ block, for instance, it corresponds to the *n*=3 state correlating to CO₂(000)+O(³P₀)].

A more detailed view of the avoided crossings among the *n*=3, 4, and 5 states of the A₁ global symmetry is given

FIG. 6. Upper panel: diagonal matrix elements of the surface Hamiltonian: $V_{00}^{3B_2}$, $V_{11}^{3A_2}$, $V_{11}^{3B_1}$ (dashed lines) and $n=3, 4, 5$ eigenenergies for the A_1 block (solid lines) as functions of the intermolecular distance. Lower panel: Weights $|c_{v\Gamma\Theta}^n|^2$ [Eq. (7)] of the three zero-order states $^3B_2v=0$, $^3A_2v=1$, and $^3B_1v=1$ in the surface state $n=4$ as functions of the intermolecular distance. Energies are in cm^{-1} and distance in angstrom. See text for discussion.

in Fig. 6. In the upper panel of this figure, it can be noticed how the crossings among the diagonal matrix elements of the surface Hamiltonian (dashed lines) for energies of about 1000 cm^{-1} become avoided ones after considering all couplings in that Hamiltonian (surface eigenenergies, in solid lines). In the lower panel of Fig. 6 we report the weights, $|c_{v\Gamma\Theta}^n|^2$, of the three zero-order or reference states, $^3B_2v=0$, $^3A_2v=1$, and $^3B_1v=1$, in the surface state $n=4$ as functions of the sectors R_j [Eq. (7)]. It can be seen that this surface state is well assigned to $^3A_2v=1$ in the region of the vdW minimum but that, for shorter intermolecular distances, there is a nonnegligible contribution of the $^3B_1v=1$ reference state due to SOC between these two zero-order states. The key point is that, around the avoided crossing between the $n=4$ and $n=3$ states at $R \sim 2.55 \text{ \AA}$, the $n=4$ state changes its character from such a mixing between the $^3A_2v=1$ and $^3B_1v=1$ states to a vibrationally relaxed state, the $^3B_2v=0$ one, in a *fairly smooth fashion*. As a consequence of this behavior, a significant state-to-state probability $P_{n=4 \rightarrow n=3}^{A_1}$, i.e., from $\text{CO}_2(010) + \text{O}(^3P_2)$ to $\text{CO}_2(000) + \text{O}(^3P_0)$, is obtained. In addition, as the $n=5$ state undergoes an avoided crossing with the $n=4$ state, a nonnegligible probability from $n=5$ to $n=3$ is also obtained. At this point, we would like to point out

that the crossings among the diagonal matrix elements are due to the different shapes of the PESs $U_\Gamma(R, \alpha)$ and that such a behavior is ultimately related to the characteristics of the $\text{CO}_2 + \text{O}$ interaction (electrostatic, induction, and exchange repulsion), depending on the orbital arrangement of the four $2p$ electrons of the oxygen atom, as already discussed in Sec. II. In addition, we find it convenient to recall the coupling scheme in the surface Hamiltonian [Eq. (9)]. Since SOC is constant with the bending angle, there is no direct coupling between zero-order states with different vibrational quantum numbers *and* spatial symmetry, for example, between $^3B_2v=0$ and $^3A_2v=1$. These states are coupled through a third zero-order state; for example, $^3B_2v=0$ couples vibrationally with $^3B_2v=1$, which then couples with $^3A_2v=1$ by spin-orbit interactions. Therefore, although pure vibrational couplings give too small quenching probabilities [Fig. 5(a)], such couplings play an essential role in the enhancement of the quenching probability once spin-orbit interactions are included in the model [Fig. 5(b)].

The results presented here provide an explanation, based on *ab initio* calculations, of the experimental observations. The kinetic energies involved in the present calculations are related to the range of temperatures of interest in the high atmosphere ($150\text{--}550 \text{ K}$). Experiments suggest that the relaxation rate does not have a strong temperature dependence in this range, but measured rates at room temperatures are much larger than estimations based on extrapolations of Center's experiments at much higher temperatures, in which the mechanism involved is clearly Landau-Teller. In accord with these observations, we have found that the spin-orbit interaction significantly enhances the vibrational quenching [Fig. 5(b)] compared to a direct V - T energy transfer process [Fig. 5(a)]. The quenching probability by means of this nonadiabatic process increases smoothly with energy; therefore a smooth temperature dependence is expected. However, the effect of SOC becomes less and less important as energy increases [compare Figs. 5(a) and 5(b) in the higher energy range]. A pure V - T process is expected to play the main role at higher energies [note in Fig. 3(b) the increase of vibrational couplings with decreasing intermolecular distance], in agreement with a high-temperature Landau-Teller behavior. In addition, a new and interesting aspect emerges from this study: vibrational quenching mediated by SOC is highly sensitive to the initial atomic angular momentum j . Moreover, we have found that $j=2 \rightarrow j=0$ and $j=2 \rightarrow j=1$ transitions play a major role in determining the fast relaxation rate of the $v=1$ level of CO_2 .

V. SUMMARY AND FINAL REMARKS

This paper reports a quantum-mechanical study of the $\text{CO}_2(010) + \text{O}(^3P)$ collision dynamics. The main goal has been to understand the high efficiency of VET at thermal energies. We have adopted a two-dimensional model in which the intermolecular distance and the bending CO_2 degree of freedom are explicitly included. On the basis of highly correlated *ab initio* calculations, we have investigated the vdW regions of the three PESs emerging from the $\text{CO}_2(^1\Sigma_g^+) + \text{O}(^3P)$ asymptote. We have found that (i) the global

minimum occurs in a $^3A_2$ spatial symmetry state and in a C_{2v} geometry; (ii) quadrupole-quadrupole and induced dipole-quadrupole contributions play a major role in determining the anisotropy of the vdW interaction along the bending CO₂ coordinate; and (iii) in the vdW region, the spin-orbit matrix elements show a rather weak dependence on the R and α coordinates, and are approximated by the $O(^3P)$ ones.

Next, we have computed the CO₂ (010) quenching probabilities as functions of collision energy and have compared the results obtained from multistate calculations [taking into account the spin-orbit mixing induced by spin-orbit coupling in $O(^3P)$] with those from separate single-surface calculations and a pure V - T energy transfer. The results clearly show (1) the dramatic influence of the spin-orbit mixing at thermal energies, (2) the high sensitivity of the VET process to the initial oxygen angular momentum j , and (3) the convergence of the two sets of calculations (with and without spin-orbit couplings) as the collisional energy increases. These conclusions are of relevance in the interpretation of the experimental measurements and aeronautical observations. In particular, since oxygen fine-structure levels can have very different populations depending on how the atoms are produced, present findings may be of interest to future experimental measurements of rate coefficients.

The purpose of this work was to give a qualitative elucidation for one of the possible mechanisms responsible for the large efficiency in the quenching of CO₂(010) by oxygen atoms colliding at thermal energies, rather than to attempt a precise determination of the rate constant. Quantitative studies require a generalization of the dynamics to higher-dimensional models with all total angular momentum states. In particular, including the θ angular coordinate may be important, and the avoided crossing between $1A''$ and $2A''$ states may have an influence on the relaxation probabilities. Work in this direction is currently underway.

ACKNOWLEDGMENTS

This work has been partially supported by the European Project No. R113-2003-506079 and the DGICYT Spanish Grant Nos. FIS2004-02461 and CTQ-2004-02415/BQU. One of the authors (M.P.d.L.-C.) was supported by the "Ramón and Cajal" Programme and another author (M.L.-P.) by the Spanish projects Nos. REN2001-3249/CLI, ESP2004-01556, and by EC FEDER funds. The calculations presented here were performed at CINECA (the SuperComputer Center of the University of Bologna), the Instituto de Matemáticas y Física Fundamental (CSIC), and CESGA (the SuperComputer Center of Galicia). One author (M.P.d.L.-C.) thanks Pavel Rosmus for stimulating discussions, James A. Dodd for providing us with his experimental results prior to publication, and Jeffrey L. Krause for suggestions on the manuscript.

APPENDIX: SELECTION RULES OF THE SPIN-ORBIT HAMILTONIAN

For C_{2v} geometries of the CO₂-O complex, there are nine spin multiplets: $^3A_2(0)$, $^3A_2(\pm 1)$, $^3B_1(0)$, $^3B_1(\pm 1)$, $^3B_2(0)$, and $^3B_2(\pm 1)$, where the numbers in parentheses indi-

cate the total spin projection quantum number M_s . The spatial symmetry and spin selection rules of the Cartesian components of the spin-orbit Hamiltonian, $\hat{H}_{L_\mu S_\mu}$ ($\mu=x, y, z$), can be derived from those of the operators $\mathbf{L} \cdot \mathbf{S}$ (see, e.g., Ref. 40); $\mathbf{L}$ and $\mathbf{S}$ are the total angular and spin momentum operators, respectively. Since the spin multiplets are eigenfunctions of S_z , the spin-orbit operator $\hat{H}_{L_z S_z}$ couples only substates for which $\Delta M_s = 0$. Since the $S_{x,y}$ operators are linear combinations of the ladder $S_\pm$ operators, which convert an M_s multiplet to an $M_s \pm 1$ multiplet, $\hat{H}_{L_x S_x}$ and $\hat{H}_{L_y S_y}$ couple states for which $\Delta M_s = \pm 1$. The spatial symmetries of the $\hat{H}_{L_\mu S_\mu}$ components can be derived from those of the L_μ operators which transform as rotations of the symmetry point group R_μ . In a molecular reference system in which xz defines the molecular plane (see Fig. 1), with z as the bisector of the OCO bending angle, one finds

$\hat{H}_{LS}$ component	Spatial symmetry	Spin selection rule
$\hat{H}_{L_x S_x}$	B_2	$\Delta M_s = \pm 1$
$\hat{H}_{L_y S_y}$	B_1	$\Delta M_s = \pm 1$
$\hat{H}_{L_z S_z}$	A_2	$\Delta M_s = 0$

Thus, $\hat{H}_{L_z S_z}$ couples only $^3B_1(M_s)$ and $^3B_2(M_s)$ spin substates, whereas $\hat{H}_{L_x S_x}$ and $\hat{H}_{L_y S_y}$ couple the $^3A_2(M_s)$ with the $^3B_1(M_s \pm 1)$ and $^3B_2(M_s \pm 1)$ multiplets, respectively. There are only three linearly independent nonzero spin-orbit matrix elements, with the remaining defined by angular momentum relationships through the Wigner-Eckart theorem.

¹R. D. Sharma and R. G. Roble, ChemPhysChem **3**, 841 (2002).

²C. J. Mertens, M. G. Mlynczak, M. López-Puertas, P. P. Wintersteiner, R. H. Picard, J. R. Winick, and L. L. Godley, Geophys. Res. Lett. **28**, 1391 (2001).

³R. L. Taylor, Can. J. Chem. **52**, 1436 (1974).

⁴R. E. Center, J. Chem. Phys. **59**, 3523 (1973).

⁵R. D. Sharma and P. P. Wintersteiner, Geophys. Res. Lett. **17**, 2201 (1990).

⁶G. M. Shved, L. E. Khvorostovskaya, I. Y. Potekhnin, A. I. Dem'Ryanikov, A. A. Kutepov, and V. I. Fomichev, Atmos. Oceanic Phys. **27**, 295 (1991).

⁷D. S. Pollock, G. B. I. Scott, and L. F. Phillips, Geophys. Res. Lett. **20**, 727 (1993).

⁸H. V. Lilenfeld, Air Force Phillips Laboratory Technical Report No. PL-TR-94-2180, 1994 (unpublished).

⁹L. E. Khvorostovskaya, I. V. Potekhnin, G. M. Shved, V. P. Ogivalov, and T. V. Uzyukova, Izve Atmos. Ocean. Phys. **38**, 613 (2002).

¹⁰M. López-Puertas, M. A. López-Valverde, C. P. Rinsland, and M. R. Gunson, J. Geophys. Res. **97**, 20469 (1992).

¹¹K. J. Castle, K. M. Kleisas, J. M. Rhinehart, E. S. H. Hwang, and J. A. Dodd, J. Geophys. Res. Space Phys. (submitted).

¹²G. B. I. Scott, D. S. Pollock, and L. F. Phillips, J. Chem. Soc., Faraday Trans. **58**, 1183 (1993).

¹³E. E. Nikitin and S. Y. Umanski, Faraday Discuss. Chem. Soc. **53**, 7 (1972).

¹⁴G. C. Schatz and M. J. Redmon, Chem. Phys. **89**, 195 (1981).

¹⁵N. M. Harvey, Chem. Phys. Lett. **88**, 553 (1982).

¹⁶R. J. Bartlett and M. J. Redmon, Air Force Rocket Propulsion Laboratory Report No. ADRPL-TR-81-27 1981 (unpublished).

¹⁷R. D. J. Froese and J. D. Goddard, J. Phys. Chem. **97**, 7484 (1993).

¹⁸A. M. Mebel, M. Hayashi, V. V. Kislov, and S. H. Lin, J. Phys. Chem. A **108**, 7983 (2004).

¹⁹A. S. Averyanov, Y. G. Khait, and Y. V. Puzanov, J. Mol. Struct. **459**, 95

- (1999).
- ²⁰C. E. Moore, *Tables of Spectra of Hydrogen, Carbon, Nitrogen, and Oxygen* (CRC, Boca Raton, FL, 1993).
- ²¹H.-J. Werner and P. J. Knowles, MOLPRO, Version 2002.6, a package of *ab initio* programs, 2002.
- ²²T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
- ²³F. M. Tao and Y. K. Pan, J. Chem. Phys. **97**, 4989 (1992).
- ²⁴B. Fernández, H. Koch, and J. Makarewicz, J. Chem. Phys. **111**, 5922 (1999).
- ²⁵S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).
- ²⁶H. B. Jansen and P. Ros, Chem. Phys. Lett. **3**, 140 (1969).
- ²⁷G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed., Molecular Spectra and Molecular Structure I (Nostrand, Princeton, 1950).
- ²⁸T. J. Lee and P. R. Taylor, Int. J. Quantum Chem. **S23**, 199 (1989).
- ²⁹The induced dipole moments have been calculated at the global minimum from the distributed multipole analysis given in the Molpro program and described in Ref. 32. We have used the RHF density matrix and assigned a radius $r=1$ a.u. to all sites.
- ³⁰A. J. Stone, Chem. Phys. Lett. **83**, 233 (1981).
- ³¹F. Negri, F. Ancilotto, G. Mistura, and F. Toigo, J. Chem. Phys. **111**, 6439 (1999).
- ³²P. J. Marshall, M. M. Szcześniak, J. Sadlej, G. Chalaśiński, M. A. ter Horst, and C. J. Jameson, J. Chem. Phys. **104**, 6569 (1996).
- ³³M. P. de Lara-Castells, Marta I. Hernández, G. Delgado-Barrio, P. Villarreal, and M. López-Puertas (unpublished).
- ³⁴A. Berning, M. Schweizer, H. J. Werner, P. J. Knowles, and P. Palmieri, Mol. Phys. **98**, 1823 (2000).
- ³⁵P. Rosmus, P. Palmieri, and R. Schinke, J. Chem. Phys. **117**, 4871 (2002).
- ³⁶I. Navizet and P. Rosmus, Chem. Phys. Lett. **411**, 457 (2005).
- ³⁷M. P. de Lara-Castells, Ph.D. thesis, Universidad Autónoma de Madrid, 1998.
- ³⁸J. C. Light and R. B. Walker, J. Chem. Phys. **65**, 4272 (1976).
- ³⁹E. B. Stechel, R. B. Walker, and J. C. Light, J. Chem. Phys. **69**, 3518 (1978).
- ⁴⁰D. Danovich and S. Shaik, J. Am. Chem. Soc. **119**, 1773 (1997).