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Experimental and theoretical investigation of the temperature dependent electronic quenching of O(1D) atoms in collisions with Kr

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The kinetics and dynamics of the collisional electronic quenching of O(1D) atoms by Kr has been investigated in a joint experimental and theoretical study. The kinetics of quenching was measured over the temperature range 50 – 296 K using the Laval nozzle method. O(1D) atoms were prepared by 266 nm photolysis of ozone, and the decay of the O(1D) concentration was monitored through vacuum ultraviolet fluorescence at 115.215 nm, from which the rate constant was determined. To interpret the experiments, a quantum close-coupling treatment of the quenching transition from the 1D state to the 3P_j fine-structure levels in collisions with Kr, and also Ar and Xe, was carried out. The relevant potential energy curves and spin-orbit coupling matrix elements were obtained in electronic structure calculations. We find reasonable agreement between computed temperature-dependent O(1D)–Rg (Rg = Ar, Kr, Xe) quenching rate constants and the present measurements for Kr and earlier measurements. In particular, the temperature dependence is well described.

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I. INTRODUCTION

The collisional de-activation of electronically excited $O(^1D)$ atoms is an important process in the chemistry of the earth’s atmosphere. The ultraviolet photolysis of ozone in the stratosphere and troposphere leads to the production of oxygen atoms in this excited state, as well as in the ground 3P state. The relatively low steady-state concentration of $O(^1D)$ atoms in the atmosphere is controlled by the rate of photolytic production and loss by collisional electronic quenching. While not as relevant for atmospheric chemistry as de-activation by and chemical reaction with molecular collision partners, the quenching of $O(^1D)$ by rare gas (Rg) atoms is a relatively simple collisional process and has attracted much interest:



In Eq. (1), the subscript j denotes that the quenched $O(^3P)$ atoms can be formed in the fine-structure levels with angular momenta $j = 2, 1$, and 0 .

The rate constant for the electronic quenching of $O(^1D)$ by the light rare gases is known to be small.¹ There have been a number of measurements of the $O(^1D)$ quenching rate constant by the heavier rare gases Ar (Refs. 2–5), Kr (Refs. 2–4), and Xe (Refs. 2 and 3) for temperatures ranging from ~ 400 K down to 50 K. Garofalo *et al.*⁶ investigated the dynamics of the quenching of $O(^1D)$ by Xe atoms in a molecular beam experiment through measurement of the differential cross section of the quenched $O(^3P)$ atoms. They found marked large-scale oscillations in the angle-resolved scattering of the $O(^3P)$ and Xe products. To interpret these intriguing observations, Dagdigian, Kłos, and Alexander⁷ carried out time-independent quantum close-coupling calculations describing this quenching process, employing computed potential energy curves and spin-orbit coupling matrix elements. Comparison of the experimental and theoretical results showed that the oscillations are caused by Stueckelberg interferences, in which the quantum phases of the multiple quenching pathways interfere constructively and destructively.

Similarly, there have been measurements of the electronic quenching of the isovalent $S(^1D)$ atom by Ar atoms⁸ and other species.^{9,10} In the recent work by Lara *et al.*,⁸ the rate constant for quenching of $S(^1D)$ by Ar was measured as a function of temperature from 298 down to 5.8 K. This rate constant was compared with a theoretical rate constant computed through quantum scattering calculations using calculated $S(^1D, ^3P)$ potential energy curves and spin-orbit matrix elements.

Previous measurements of the rate constant for electronic quenching of $O(^1D)$ by Kr have been reported down to a temperature of 113 K.² In the present study, we report measurement of this

rate constant from 50 to 296 K. As a compliment to our measurement and previous determinations of the rate constants for the quenching of $O(^1D)$ by the heavy rare gases, we have also computed integral cross sections and rate constants for quenching by Ar, Kr, and Xe. We employed the previously computed⁷ $O(^1D, ^3P)$ potential energy curves and spin-orbit matrix elements and have carried out here similar calculations for $O(^1D, ^3P)$ -Kr and $O(^1D, ^3P)$ -Ar. We find that the energy-dependent cross sections for all three collision pairs show many sharp peaks, that are most prominent for Kr and Ar as the collision partner. We show that these peaks are resonances that are quasi-bound by the centrifugal barrier at the highest partial wave that contributes to the quenching cross section.

This paper is organized in the following manner. Section II presents the experimental method and results on the measurement of the $O(^1D)$ quenching rate constant by Kr. Sections III A and III B describe the *ab initio* calculation of the $O(^1D, ^3P)$ -Kr, Ar potential energy curves and spin-orbit matrix elements and the details about the scattering calculations, respectively. Section III C 1 presents and interprets the computed cross sections for electronic quenching of $O(^1D)$ by Kr and Ar. The computed $O(^3P)$ fine-structure relative populations formed in the quenching by Kr are compared with a measurement by Matsumi *et al.*¹¹ in Sec. III C 2. Section III C 3 presents computed temperature-dependent rate constant for the quenching of $O(^1D)$ by Ar, Kr, and Xe and compares these with the experimental measurement. A discussion follows in Sec. IV.

II. EXPERIMENT

A. Methods

The experimental part of this work was performed using a supersonic flow (Laval nozzle) reactor operating in continuous mode. A detailed description of the apparatus can be found in earlier work.^{12,13} Three different axisymmetric nozzles were employed during this investigation, allowing generation of flows at three different fixed low temperatures (50 K, 75 K, and 127 K), each with a uniform density profile and a constant velocity. Although we have a range of Laval nozzles available with Ar, N_2 and N_2/SF_6 mixtures as the carrier gases, only Ar based nozzles could be used in this study due to the efficient non-reactive quenching of $O(^1D)$ by N_2 below room temperature.^{5,14} The supersonic flow characteristics of these nozzles are presented in Table 1 of Grondin *et al.*⁵ and were obtained in separate calibration experiments. In these experiments, the Mach number

(the ratio of the flow velocity to the speed of sound for the specific carrier gas at the local temperature) was determined from standard isentropic flow equations relating the stagnation pressure (reservoir pressure) and the impact pressure obtained with a Pitot tube inserted into the supersonic flow. Measurements were also performed at room temperature by operating without a nozzle and by throttling the pumps to reduce the flow velocity, thereby eliminating temperature and pressure gradients within the reactor.

Electronically excited state $O(^1D)$ atoms [in addition to coproducts $O_2(a^1\Delta_g)$] were created directly in the supersonic flow by the 10 Hz pulsed laser photolysis of ozone (O_3) at 266 nm with energies around 25 mJ, in a 6 mm diam beam. This process is known to occur with a quantum yield of approximately 0.9 (Ref. 15) at this wavelength, with $O(^3P)$ and $O_2(X^3\Sigma_g^-)$ as minor photolysis products. Ozone was generated by the ultraviolet (UV) irradiation by a high-pressure mercury lamp of pure O_2 flowed continuously into a quartz cell upstream of the reactor. The cell itself was maintained at high pressure (700 Torr), thereby promoting O_3 formation through the $O(^3P) + O_2 + M$ recombination reaction. The effluent of the cell (essentially O_2 with a small percentage of O_3) was then mixed with the carrier gas Ar and the co-reagent gas Kr and carried into the Laval nozzle reservoir.

$O(^1D)$ atoms were probed directly in this work by pulsed vacuum ultraviolet laser induced fluorescence (VUV LIF) through the $3s\ ^1D - 2p\ ^1D$ transition at 115.215 nm. The procedure to generate tuneable VUV light, as well as to detect resonant VUV emission, are described in previous work.^{5,16,17}

The $O(^1D)$ VUV LIF signal was followed as a function of delay time between photolysis and probe lasers, with a boxcar integration system coupled to a PC used for signal acquisition and processing. Both lasers and the acquisition electronics were synchronized using a digital delay generator. A total of 30 laser shots were recorded at each time interval, with a least 70 time intervals used to establish the $O(^1D)$ decay profiles. In addition, at least 15 negative time points (that is with the probe laser firing prior to the photolysis laser) were recorded for each decay profile to set the baseline level. The gases O_2 (99.999%), Ar (99.999%), Kr (99.999%) and Xe (99.998%) were all used with no further purification during the present experiments. The co-reagent Kr concentrations were determined from the product of its flow ratio (F_{Kr} / F_{tot}) and the supersonic flow density. Calibrated mass flow controllers were used to drive the gas flows, with calibration factors determined by a pressure rise at constant volume method for the specific gas used.

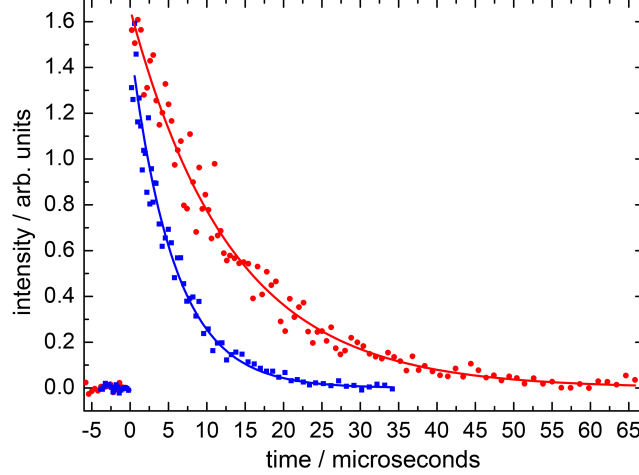


FIG. 1. $O(^1D)$ VUV LIF signal as a function of delay time recorded at 127 K. (red solid circles) without added Kr ($[Ar] = 1.26 \times 10^{17} \text{ cm}^{-3}$); (blue solid squares) with $[Kr] = 1.48 \times 10^{16} \text{ cm}^{-3}$. The solid red and blue lines represent the best fit derived by fitting a single exponential decay function to the experimental data points. Pseudo-first-order rates were extracted from the time constant of the fit.

B. Results

The concentration of Kr used in the experiments was always much greater than the $O(^1D)$ concentration ($[O_2]_{\text{max}} = 7.0 \times 10^{13} \text{ cm}^{-3}$ with $[Kr]_{\text{min}} = 1.3 \times 10^{15} \text{ cm}^{-3}$) so that the pseudo-first-order approximation was valid at all temperatures. Under these conditions the $O(^1D)$ VUV LIF signal decreased exponentially as a function of time according to the formula $I_t = I_0 \exp(-k't)$, where I_t and I_0 are the time dependent and initial $O(^1D)$ VUV LIF signals, respectively, and t is the time. The quantity k' is the pseudo-first-order loss rate for $O(^1D)$ atoms and contains contributions from several different processes:



such that $k' = k_{O(^1D)-Kr}[Kr] + k_{O(^1D)-Ar}[Ar] + k_{O(^1D)-O_2}[O_2] + k_{O(^1D)-O_3}[O_3] + k_{\text{diff}}$. Some typical $O(^1D)$ decay curves recorded at 127 K in the presence and absence of Kr are shown in Fig. 2.

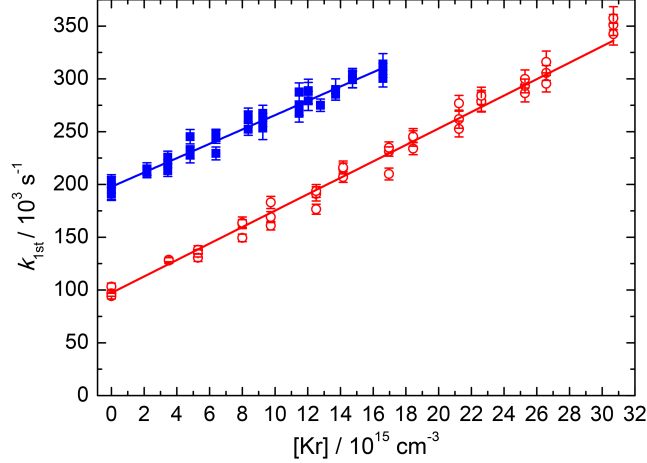


FIG. 2. Measured pseudo-first-order rate constants as a function of excess Kr concentration. Red open circles: data recorded at 296 K; blue solid squares: data recorded at 50 K. The solid red and blue lines represent weighted fits to the respective data sets (see text for details), yielding the second-order rate constant from the slope.

The $O(^1D)$ signal decays rapidly even in the absence of Kr [$k' = (7.58 \pm 0.19) \times 10^4 \text{ s}^{-1}$ for the red data points shown in Fig. 1] due to the efficient relaxation of $O(^1D)$ atoms by the carrier gas Ar with a roughly temperature independent rate constant $k_{O(^1D)-Ar} = 6.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ (Refs. 2 and 5). In this particular example, $[Ar] = 1.26 \times 10^{17} \text{ cm}^{-3}$ [see Table 1 of Grondin *et al.* (Ref. 5)], so that $k_{O(^1D)+Ar}[Ar] = 7.56 \times 10^4 \text{ s}^{-1}$. The contributions of processes (4) – (6) are clearly quite negligible with respect to processes (2) and (3) in this example and in all other decays, as already argued by Grondin *et al.*⁵ When Kr is added to the system ($[Kr] = 1.48 \times 10^{16} \text{ cm}^{-3}$ for the blue data points in Fig. 1), $O(^1D)$ atoms decay much more rapidly, with a pseudo first-order rate constant $k' = (1.78 \pm 0.8) \times 10^5 \text{ s}^{-1}$.

Pseudo-first-order rate constants were determined over a wide range of different Kr concentrations at each temperature. A plot of the pseudo-first-order rate constants against the corresponding Kr concentrations yielded the second-order rate constant from a weighted linear least-squares fit to the data. The second order plots obtained at 50 K and at 296 K are shown in Fig. 2.

In these experiments, the fits were weighted by the uncertainty derived by exponential fits to first-order decay profiles such as those shown in Fig. 1. The large y-axis intercepts of these second-order plots represent $O(^1D)$ loss essentially through reaction (3), as described above. In addition, since large Kr flows were required in some of these experiments due to the relatively slow $O(^1D)$ quenching rate, it was necessary to reduce the Ar flow rate to maintain a constant reservoir pressure

(a prerequisite for experiments of this type for the Laval nozzle calibrations to be considered valid). Consequently, as $[\text{Ar}]$ decreased slightly with increasing $[\text{Kr}]$, a small correction was applied to the $\text{O}(^1D)$ first-order decay rates to compensate for the reduced relaxation by Ar. This correction was given by the following formula: $([\text{Ar}]_0 - [\text{Ar}]_{\text{Kr}}) k_{\text{O}(^1D)-\text{Ar}}$, where $[\text{Ar}]_0$ is the nominal Ar density for the specific nozzle, $[\text{Ar}]_{\text{Kr}}$ is the Ar density with added Kr, and $k_{\text{O}(^1D)-\text{Ar}}$ is the measured second-order rate constant for $\text{O}(^1D)$ removal by Ar.^{2,5} Adding this correction to the measured pseudo-first-order rate constants resulted in an increase of less than 10% to the second-order rate constants. The corrected second-order rate constants obtained for the $\text{O}(^1D) + \text{Kr}$ reaction are presented in Table I, with other relevant information, and are displayed as a function of temperature in Fig. 3 along with earlier results.

TABLE I. Measured second-order rate constants for the $\text{O}(^1D) + \text{Kr}$ quenching reaction.

T / K	N^a	$[\text{Kr}] / 10^{15} \text{ cm}^{-3}$	$k_{\text{O}(^1D)-\text{Kr}} / 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
296	42	0–26.6	7.8 ± 0.8^c
127 ± 2^b	40	0–13.5	7.3 ± 0.8
75 ± 2	36	0–12.2	6.1 ± 0.7
50 ± 2	39	0–16.6	6.8 ± 0.7

a Number of individual measurements.

b Uncertainties in the calculated temperatures represent the statistical (1σ) errors obtained from Pitot tube measurements of the impact pressure as a function of distance from the Laval nozzle.

c Uncertainties on the measured rate constants represent the combined statistical (1σ) and estimated systematic (10%) errors.

III. THEORY

A. Electronic structure calculations

In order to perform quenching scattering calculations, we need information on the potential energy curves (PEC's) and spin-orbit matrix elements for the interaction of closed-shell 1S rare gas atoms with the oxygen atom in its ground 3P and first excited 1D electronic states. We employ similar computational methodology to that described in earlier work on $\text{O}(^1D, ^3P) - \text{Xe}$ quench-

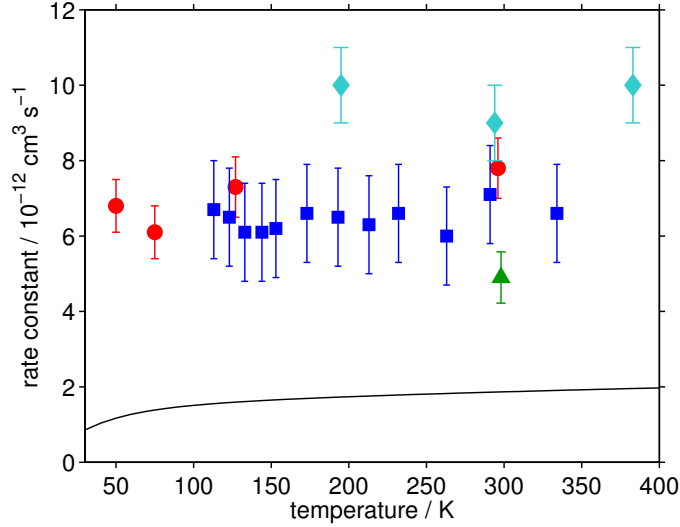


FIG. 3. Rate constants for the $\text{O}(^1D) + \text{Kr}$ quenching reaction as a function of temperature. Experimental results: red filled circles: this work; blue squares, Davidson *et al.* (Ref. 2); green triangle, Shi and Barker (Ref. 3); cyan diamonds, Blitz *et al.* (Ref. 4). Computed value: black line, this work.

ing by Dagdigian *et al.*⁷ Similarly to O–Xe, the O–Kr and O–Ar interactions with $\text{O}(^1D)$ and $\text{O}(^3P)$ atoms will give rise to three and two unique non-relativistic PEC’s, respectively. The non-relativistic $\text{O}(^3P)$ –Rg interaction is described by three (two unique) adiabatic curves, one of $^3\Sigma^-$ symmetry and the second (doubly degenerate) of $^3\Pi$ symmetry. The $\text{O}(^1D)$ –Rg non-relativistic interaction is described by five PEC’s (three unique) belonging to $^1\Sigma^+$, $^1\Pi$ (doubly degenerate) and $^1\Delta$ (doubly degenerate) representations. We use the MOLPRO suite of programs¹⁸ to obtain all of these PEC’s from first principles calculations.

As in our work on O–Xe quenching,⁷ we perform two sets of *ab initio* calculations of the O–Kr and O–Ar PEC’s. The first set is based on the multi-reference configuration interaction with single and double excitations^{19,20} method with a correction for quadruple excitations²¹ (MRCISD+Q). The MRCISD+Q calculations also provide necessary spin-orbit coupling terms between all the electronic states considered in the O–Rg systems. The second set employs the spin unrestricted coupled-cluster method with single, double and non-iterative triple excitations [UCCSD(T)]. The UCCSD(T) method describes well all the potential energy curves except the one for the $^1\Pi$ state.⁷ For that state we will use the PEC obtained from the set of MRCISD+Q calculations.

We perform all-electron *ab initio* calculations. In these, we have to account for the scalar relativistic effects that can be important for the Kr atom. For this reason we employ the aug-

mented correlation-consistent polarized quadruple and quintuple zeta atomic basis sets designed for Douglas-Kroll relativistic calculations [aug-cc-pvqz-DK in the MRCISD and aug-cc-pv5z-DK in the UCCSD(T) calculations].

The MRCISD calculations were started from the state-averaged multiconfiguration self consistent field calculations (MCSCF). The active space employed in the MCSCF calculations included 15 core orbitals, 5 closed (doubly occupied), but correlated, orbitals, and three active p orbitals of the oxygen atom. The states of Σ , Π and Δ symmetry were obtained by applying the projection operator methodology implemented in the MOLPRO program, ensuring that the wavefunctions are eigenvectors of the L^2 operator.

To determine the UCCSD(T) interaction energies that describe the PEC's, we use the supermolecular method in which we correct for the basis set superposition error by applying the counterpoise procedure of Boys and Bernardi²² (all total energies calculated in the dimer basis set). In the case of the MRCI calculations, the lack of size-consistency of the method is remedied by subtracting the interaction energy at a large ($R = 30a_0$) O-Rg separation. The correction for quadruple excitations in the MRCI calculations accounts, partially, for higher excitations, and helps to reduce the size-consistency error.

Figure 4 displays the potential energy curves for all the $O(^3P, ^1D)$ -Kr, Ar states. As in the case of O-Xe,⁷ we see that the $^1\Sigma^+$ state is the most strongly bound singlet state for both complexes. For this state, the O $2p$ orbital aligned along the internuclear axis is vacant. The binding energy of this state is the smallest for O-Ar, significantly larger for O-Kr, and larger still for O-Xe [$D_e = 13365.8 \text{ cm}^{-1}$].⁷ The other electronic states have shallow van der Waals wells. The $^1\Delta$ and $^3\Sigma^-$ states are the most repulsive; for these states the O $2p$ orbital aligned along the internuclear axis is doubly occupied.

The values of the dissociation energies D_e and equilibrium internuclear separations R_e for the computed O-Kr and O-Ar triplet and singlet states are listed in Table II. We compare the values of D_e and R_e the triplet states calculated in this work with empirically determined values of these parameters derived by Aquilanti *et al.*²³ The latter were obtained in molecular beam experiments employing magnetically state-selected $O(^3P)$ atoms. The agreement of the computed and experimental values is quite good.

There have been a number of previous calculations on the triplet states of O-Kr and O-Ar.²⁴⁻³⁰ The most recent of these calculations on O-Kr, which used the RCCSD(T) method with a variety of basis sets obtained the values $R_e = 7.417a_0$ and $D_e = 58.3 \text{ cm}^{-1}$ for the $^3\Sigma^-$ state and $R_e =$

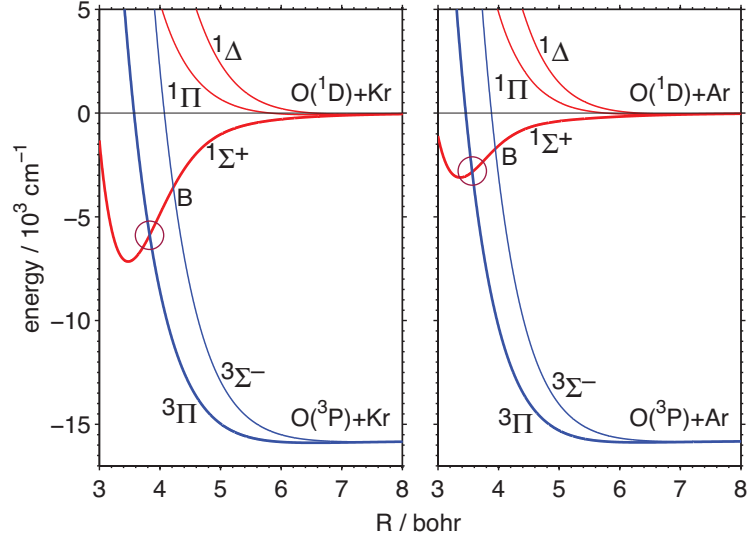


FIG. 4. Potential energy curves for the interaction of $O(^3P, ^1D)$ with Kr (left-hand panel) and Ar (right-hand panel) in the absence of spin-orbit coupling: UCCSD(T) calculations, except for the MRCISD+Q calculation for the $^1\Pi$ state. The curves of states of singlet and triplet spin multiplicity are plotted in red and blue, respectively. The predominant spin-orbit coupling occurs between the $^1\Sigma^+$ and $^3\Pi_{\Omega=0^+}$ curves, designated by the small magenta circle. An additional crossing between the $^1\Sigma^+$ and $^3\Sigma^-$ curves is marked with a "B". There is one additional crossing [$^1\Pi - ^3\Sigma^-$], but this occurs above the plotted energies.

TABLE II. Computed dissociation energies [D_e , in cm^{-1}] and equilibrium internuclear separations [R_e , in a_0] for the electronic states of OKr and OAr.

State	OKr		OAr		Empirical OKr ^a		Empirical OAr ^a	
	D_e	R_e	D_e	R_e	D_e	R_e	D_e	R_e
$O(^3P) + Rg$								
$^3\Sigma^-$	54.3	7.453	46.3	7.201	71.0 ± 7.1	7.65 ± 0.15	58.1 ± 5.8	7.28 ± 0.14
$^3\Pi$	100.2	6.540	82.7	6.349	105.7 ± 10.6	6.75 ± 0.14	83.9 ± 8.4	6.52 ± 0.13
$O(^1D) + Rg$								
$^1\Sigma^+$	7150.7	3.476	3129.2	3.366	-	-	-	-
$^1\Pi$	81.7	6.615	61.6	6.524	-	-	-	-
$^1\Delta$	54.4	7.342	46.9	7.082	-	-	-	-

^a Potentials derived from the scattering experiments of Aquilanti *et al.* (Ref. 23).

$6.516a_0$ and $D_e = 100.7 \text{ cm}^{-1}$ for the $^3\Pi$ state. Our values are in good agreement with these results.

As noted previously,⁷ there are nine and five spin projection states for the oxygen 3P and 1D states, respectively. The matrix elements of the 14×14 spin-orbit matrix expressed in a Cartesian basis were calculated at the MRCISD level using the MOLPRO suite of programs.^{18,31} There are two unique matrix elements describing the spin-orbit coupling within the 3P state and five such matrix elements describing the spin-orbit coupling between the 1D and 3P states. These matrix elements, which are defined in Ref. 7, for O–Kr and O–Ar are plotted in Fig. 5. We see in Fig. 5 that the matrix elements deviate significantly from their asymptotic values when the internuclear separation R becomes small. A similar effect was seen for O–Xe; however, the deviation from the asymptotic values was much larger. We do see in Fig. 5 that the spin-orbit matrix elements for small R are larger for Kr than for Ar. We certainly expect that the spin-orbit matrix elements would follow in the order O–Ar < O–Kr < O–Xe, going down the column of the rare gases in the periodic table.

The quenching of O(1D) by a rare gas can, in principle, be mediated by three different singlet-triplet crossings, namely between (1) the $^1\Sigma^+$ and $^3\Pi$ states, (2) the $^1\Sigma^+$ and $^3\Sigma^-$ states, and (3) the $^1\Pi$ and $^3\Sigma^-$ states. Based on our previous work on O–Xe,⁷ we expect that the first crossing, which lies considerably below the O(1D) + Rg asymptote (denoted with small magenta circles in Fig. 4) will dominate the quenching by Kr and Ar. The second crossing also lies below the singlet asymptote and can also contribute to the quenching. In O–Xe, the third crossing lies $\sim 2000 \text{ cm}^{-1}$ above the singlet asymptote and contributes, in this system, to quenching only at high collision energies.⁷ By contrast for O–Kr and O–Ar, this crossing lies much higher above the singlet asymptote, out of the range of the energies considered here (plotted in Fig. 4).

B. Scattering formalism

The formalism for quantum scattering to describe the collision-induced $^1D \rightarrow ^3P$ transition in the oxygen atom has been presented previously.^{7,32} We provide a brief description here. The Hamiltonian for the O–Rg system can be written in atomic units ($\hbar = 1$) as

$$\hat{H}(\mathbf{R}, q) = -\frac{1}{2\mu R^2} \frac{d^2}{dR^2} + \frac{\mathbf{I}^2}{2\mu R^2} + \hat{H}_{\text{el}}(q) + V(R, q) + \hat{H}_{\text{so}}(R, q) \quad (7)$$

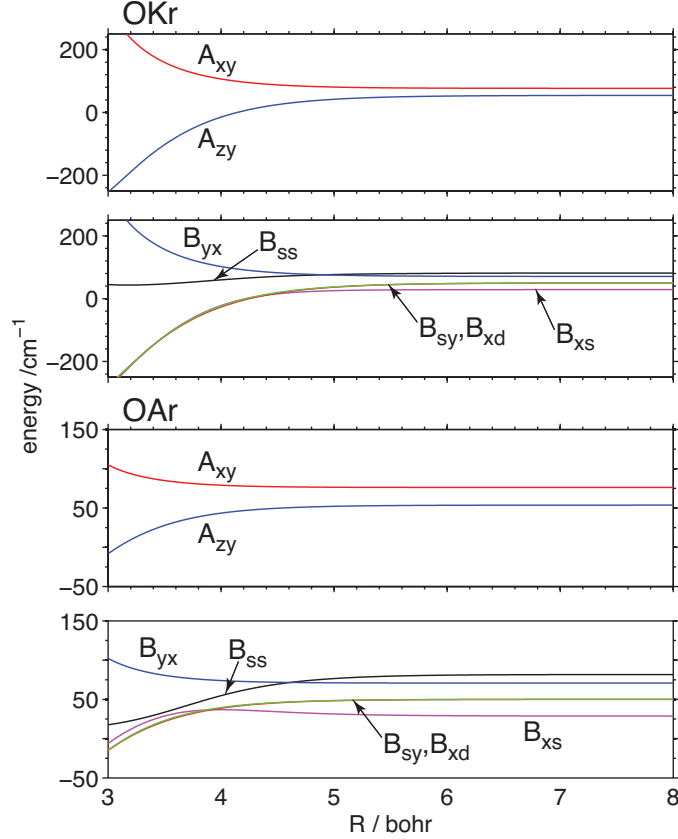


FIG. 5. Spin-orbit matrix elements between OKr (top panels) and OAr (bottom panels) wave functions. Matrix elements between 3P projection states: $A_{xy} \equiv \langle ^3\Pi_x | L_z S_z | ^3\Pi_y \rangle$ and $A_{zy} \equiv \langle ^3\Pi_x | L_x S_x | ^3\Sigma \rangle$. Matrix elements between 3P and 1D projection states: $B_{yx} \equiv \langle ^3\Pi_y | L_z S_z | ^1\Pi_x \rangle$, $B_{ss} \equiv \langle ^3\Sigma | L_z S_z | ^1\Sigma \rangle$, $B_{xs} \equiv \langle ^3\Pi_x | L_y S_y | ^3\Sigma \rangle$, $B_{sy} \equiv \langle ^3\Sigma | L_y S_y | ^1\Pi_y \rangle$, and $B_{xd} \equiv \langle ^3\Pi_x | L_x S_x | ^1\Delta \rangle$.

where \mathbf{R} is the vector separating the atoms, q represents the electronic coordinates, μ is the collision reduced mass, and \mathbf{l} is the orbital angular momentum. The term $\hat{H}_{el}(q)$ is the energy of the isolated $O(^3P, ^1D)$ atom, and $V(R, q)$ is the electrostatic interaction between the atoms; the latter approaches zero as R becomes larger. The term $\hat{H}_{SO}(R, q)$ describes the spin-orbit interaction in the O atom; this term is affected by the approach of the rare gas atom.

The electronic part of the scattering wave function at large R is described by the quantum numbers L , S , and j , namely the electronic, spin, and total angular momentum, respectively, of the oxygen atom. We express the scattering wave function in the space frame (SF) as

$$|LS j l J M\rangle = \sum_{m_j m_l} \langle j m_j l m_l | j l J M \rangle |LS j m_j\rangle |l m_l\rangle \quad (8)$$

where J and M are the total angular momentum and its space-fixed projection, respectively, and l

is the orbital angular momentum.

The matrix elements of $V(R, q)$ and $\hat{H}_{\text{SO}}(R, q)$ are computed in the body frame, as described in Sec. III A. The body-frame (BF) basis functions can be transformed to the SF basis with the following transformation, which has been described in detail previously:³³

$$|LS j l J M\rangle = \left(\frac{[l][J]}{4\pi} \right)^{1/2} (-1)^J \sum_{\Omega} (-1)^{\Omega} \begin{pmatrix} l & j & J \\ 0 & \Omega & -\Omega \end{pmatrix} D_{M\Omega}^{J*}(\phi, \theta, 0) |LS j \Omega\rangle \quad (9)$$

Here, $[x] = 2x + 1$, the D is a rotation matrix element,³⁴ and Ω is the body-frame projection of J and j . The spin-orbit operator mixes the $\Omega = \pm 2$ components of the isolated 3P and 1D states; this mixing must be taken into account in describing the asymptotic atomic states. We compute the spin-orbit interaction in Eq. (7) as $\hat{H}_{\text{SO}}(R, q) - \hat{H}_{\text{SO}}(R = \infty, q)$ so that this interaction goes to zero for large R .

The matrix elements of $V_{\text{el}}(R, q) \equiv V(R, q) + \hat{H}_{\text{SO}}(R, q)$ are diagonal in Ω in the BF basis. Using Eq. (9), we can express the SF matrix elements of $V_{\text{el}}(R, q)$ in the following way:

$$\begin{aligned} \langle L'S' j' l' J M | V_{\text{el}}(R, q) | LS j l J M \rangle &= ([l'][l])^{1/2} \\ &\times \sum_{\Omega} \begin{pmatrix} l' & j' & J \\ 0 & \Omega & -\Omega \end{pmatrix} \begin{pmatrix} l & j & J \\ 0 & \Omega & -\Omega \end{pmatrix} \langle L'S' j' \Omega | V_{\text{el}}(R, q) | LS j \Omega \rangle \end{aligned} \quad (10)$$

The BF matrix elements of $V(R, q)$ for the 3P state are given in Ref. 33; these matrix elements for the 1D state equal

$$\langle LS \Omega | V(R, q) | LS \Omega \rangle = V_{\Lambda=\Omega}(R) \quad (11)$$

The BF matrix elements of $\hat{H}_{\text{SO}}(R, q)$ are given in the Appendix of Ref. 7.

Time-independent quantum scattering calculations for the O–Rg systems were performed with the HIBRIDON suite of programs.³⁵ Convergence of the cross sections was checked with respect to the sector width in the radial integration and the number of partial waves. Partial waves up to $J = 280$ were included in the calculations. The cross sections were computed on a 1 cm^{-1} spacing for total energies less than 2000 cm^{-1} and a spacing of 2 cm^{-1} for energies between 2000 and 5000 cm^{-1} .

C. Calculations

1. Cross Sections

Figure 6 displays the integral cross sections for formation of the individual 3P_j fine-structure levels, as well as the sum of these fine-structure dependent cross sections, as a function of collision energy for the quenching of $O(^1D)$ by Kr and Ar. The cross sections show slow oscillations in magnitude as a function of the collision energy, as well as superimposed sharp features. This behavior is similar to what we observed for the energy dependence of the O–Xe quenching cross sections,⁷ except that the sharp features are much more prominent for O–Kr and O–Xe. It can be seen that over the range of collision energies investigated only the 3P_j , $j = 2$ and 0, fine-structure states are significantly populated in the quenching of $O(^1D)$ by Kr and Xe. This is in contrast to the quenching of $O(^1D)$ by Xe,⁷ for which the 3P_1 state is formed with significant yield for collision energies greater than approximately 2000 cm^{-1} . For this system, quenching to form the 3P_1 state can occur through the crossing of the $^1\Pi$ and $^3\Sigma^-$ states. As discussed in Sec. III A, this crossing lies too high to be accessible in O–Kr and O–Ar collisions.

The sharp features in the energy dependent cross sections plotted in Fig. 6 are intriguing. Similar sharp features were observed in computed energy dependent cross section for intramultiplet transitions in collisions of $O(^3P_j)$ fine-structure levels with rare gases.²⁹ Figure 7 displays a plot, over a narrower energy range, of the energy dependent cross sections, summed over the $O(^3P_j)$ fine-structure levels, for the quenching of $O(^1D)$ by Kr. Since the sharp features appear for each final level, for clarity we plot only the cross section summed over the fine-structure levels. We see that there are several lines of features, with the widths within a given series increasing as a function of the collision energy.

To gain insight into the origin of these features, it is convenient to consider the simpler 2-state model that we employed to understand the origin of oscillations in the differential cross section for the electronic quenching of $O(^1D)$ by Xe.⁷ As in the case of $O(^3P)$ –Xe, the dominant coupling enabling the quenching is between the $^1\Sigma^+$ state and the $\Omega = 0^+$ component of the $^3\Pi$ state. We consider just these two diabatic potential energy curves, along with a Gaussian coupling (in units of cm^{-1}):

$$V_{12}(R) = 103 \exp[-\alpha(R - R_c)^2] \quad (12)$$

where $R_c = 3.825a_0$ is the crossing between the two diabatic curves (circled in magenta in the

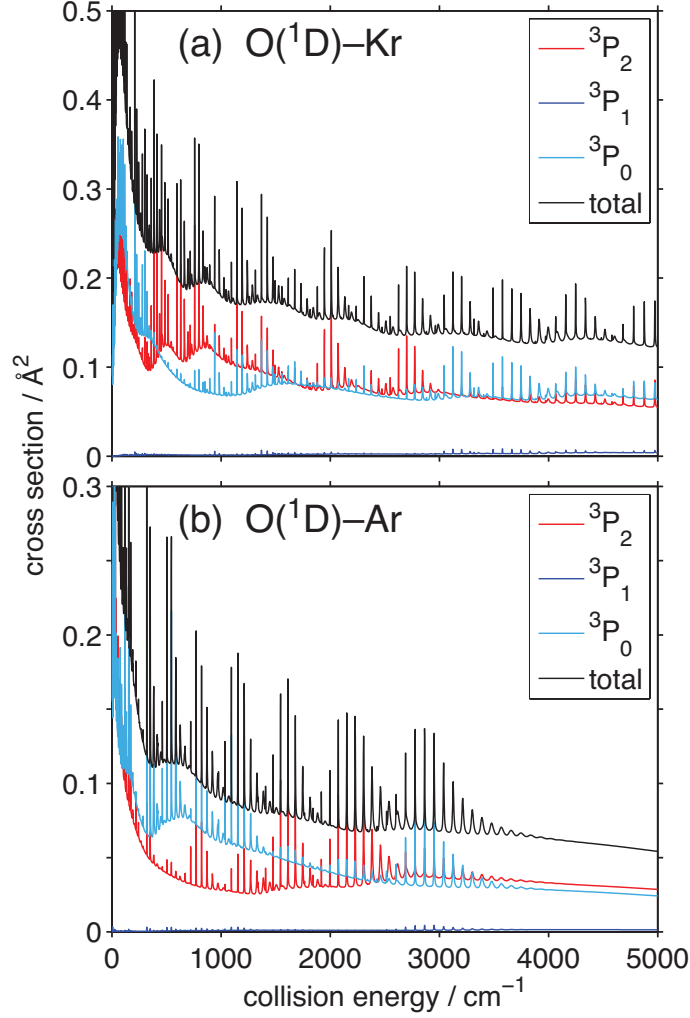


FIG. 6. Integral cross sections for the quenching of $O(^1D)$ by (a) Kr and (b) Ar to the individual $O(^3P_j)$ fine-structure as a function of the collision energy. Also plotted is the cross section summed over the fine-structure levels.

left-hand panel of Fig. 4), $V_{12}(R)$ at $R = R_c$ was set to the value of the spin-orbit coupling between the two curves, and the width parameter α was set to $1.0a_0$.

Figure 8(a) presents a plot of the energy dependent quenching cross section computed within this 2-state model. The energy dependence of the cross section is remarkably similar to the cross sections computed with the full set of potentials. Again, we see a number of series of sharp features. The magnitude of the cross sections is larger than in the full calculations, but the size of the cross sections in the 2-state model is arbitrary and just depends upon the strength and range of the assumed coupling.

Figure 8(b) displays an expanded plot over the narrow energy range. The widths of the features

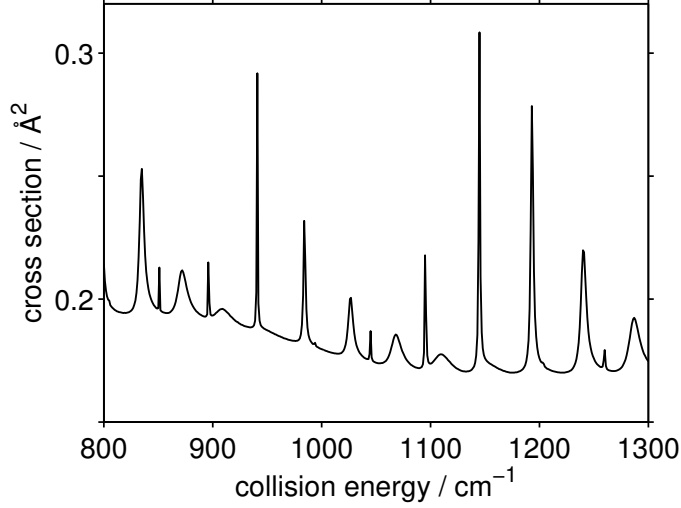


FIG. 7. Expanded plot of the integral cross section for the quenching of $O(^1D)$ by Kr, summed over the $O(^3P_j)$ fine-structure levels as a function of the collision energy.

within a given series are seen to increase with increasing energy. It is useful and revealing to plot the partial cross sections, namely the cross section for each partial wave of total angular momentum J for energies on and off a given feature. Figure 9 displays partial cross sections for a collision energy of 1135 cm^{-1} , at a sharp feature, and a slightly lower collision energy of 1110 cm^{-1} . For both collision energies, the partial cross sections drop abruptly to zero at the highest partial wave. Above this value of the total angular momentum J , the centrifugal barrier becomes greater than the collision energy, and the crossing region can no longer be accessed. Tunneling is not important for these systems since the reduced mass is relatively large ($\mu = 13.42 \text{ amu}$).

We see that for the sharp feature at a collision energy of 1135 cm^{-1} the partial cross section for the highest partial wave ($J = 106$) makes the dominant contribution to the integral cross section and yields a much higher integral cross section than at the slightly lower collision energy. We have examined the partial cross sections for collision energies corresponding to many of the sharp features. In all cases, the partial cross sections for the highest partial wave makes the dominant contribution to the integral cross section. The largest total angular momenta J , that make the dominant contribution, are indicated for the peaks in Fig. 8.

We can show that the sharp features are due to resonances by examining the scattering wave functions. Figure 10 displays the $^1\Delta$ component of the scattering wave function for several partial waves at a collision energy of 1135 cm^{-1} , which is the energy of one of the sharp features in Fig. 8. The bottom panel of Fig. 10 displays the potential energy curves of the $^1\Sigma^+$ and $^3\Pi$ states, as

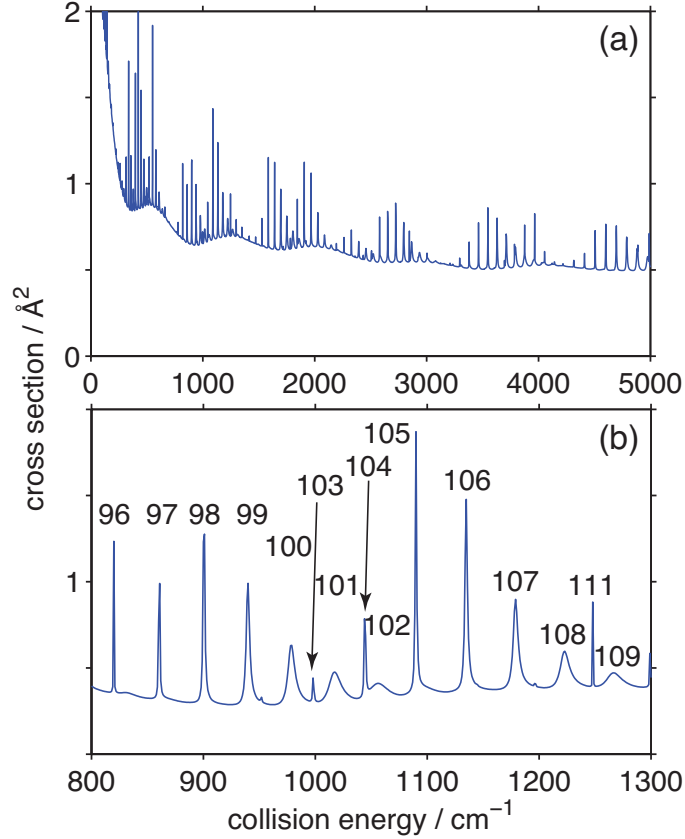


FIG. 8. (a) Integral cross sections for the quenching of $\text{O}(^1D)$ by Kr as a function of the collision energy within the 2-state model. (b) Plot with an expanded collision energy range; the numbers above the peaks indicate the total angular momentum J of the dominant, and highest, partial wave contributing to the integral cross section at that energy.

well as the adiabatic potentials for total angular momentum $J = 106$, which makes the dominant contribution to the integral cross section at this energy. The collision energy is indicated in this panel with a horizontal line. It can be seen that this energy is very slightly smaller than the height of the centrifugal barrier.

It is interesting to compare the amplitude of the $^1\Delta$ component of the scattering wave function inside and outside the centrifugal barrier. For the highest, and dominant, partial wave ($J = 106$) that contributes to the integral cross section, the amplitude is considerably enhanced inside the barrier. This implies that the collision complex is quasi-bound, and hence there is a greater probability for quenching to the 3P state. For a lower partial wave, $J = 101$, the centrifugal barrier is significantly less than the collision energy, and the amplitude of the $^1\Delta$ component is slightly smaller inside the barrier than outside. The next partial wave, $J = 107$, after the dominant partial

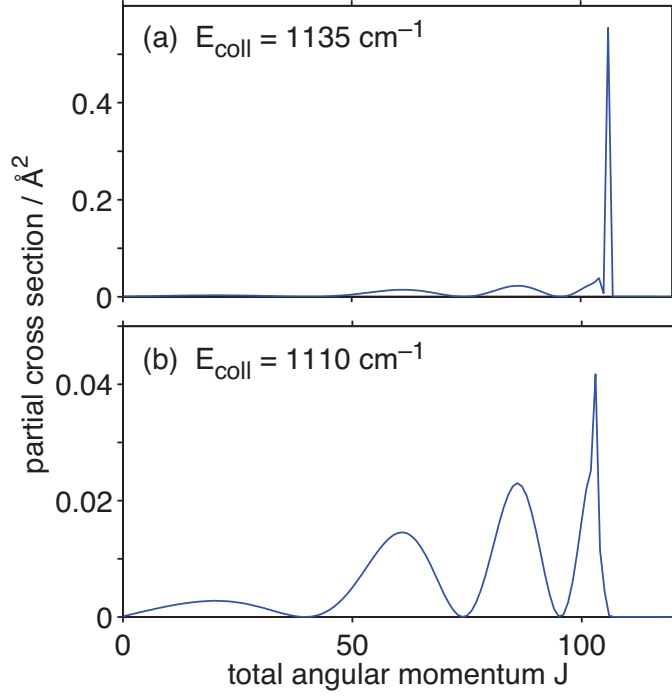


FIG. 9. (a) Partial cross sections as a function of the total angular momentum J for the quenching of $\text{O}(^1D)$ by Kr as a function of the collision energy within the 2-state model at collision energies of (a) 1135 cm^{-1} and (b) 1110 cm^{-1} .

wave ($J = 106$), is seen in Fig. 10 to have a very small amplitude inside the barrier. Hence, this partial wave contributes negligibly to the electronic quenching. As noted previously, the reduced mass of the OKr collision pair is large enough that tunneling is not significant.

We have examined the scattering wave functions for collision energies corresponding to other peaks in the integral cross sections. In all cases, the amplitude of the $^1\Delta$ component of the scattering wave function at these energies is enhanced relative to its amplitude outside the barrier. We can conclude that the peaks in the energy dependent quenching cross sections are due to resonances. The lifetimes of the quasi-bound states are proportional to the inverse of the widths of the peaks; the increasing widths of the resonances within a given series implies that the lifetime of the quasi-bound complex is correspondingly decreasing. The number of nodes of the the $^1\Delta$ component inside the barrier is the same (and is equal to 13) for the peaks marked in Fig. 8(b). Hence, these resonances can be described as representing different rotational levels of a quasi-bound vibrational level. We have not carried out an analysis of all the resonances in the energy-dependent

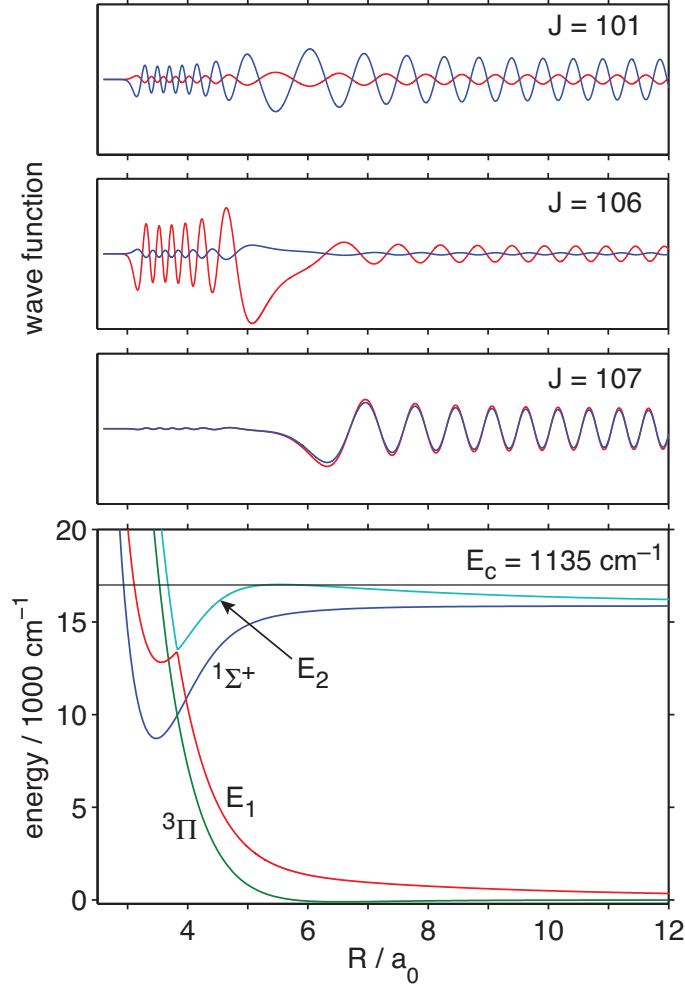


FIG. 10. Top three panels: The $^1\Delta$ component of the scattering wave function for several partial waves ($J = 101, 106$, and 107) for a collision energy of 1135 cm^{-1} . Bottom panel: Potential energy curves for the $^1\Sigma^+$ and $^3\Pi$ states in the 2-state model and adiabatic energies E_1 and E_2 for total angular momentum $J = 106$. Also plotted in the bottom panel is the total energy for a collision energy $E_c = 1135 \text{ cm}^{-1}$.

cross section.

It can be inferred from Figs. 6, 7, and 8 that the strength of the resonances, as reflected in the integral of the individual resonances, varies as a function of the collision energy. This reflects the tuning of the height of the centrifugal barrier for the last partial wave relative to the collision energy. These energies must be closely matched in order to have resonance-enhancement of the quenching cross section.

2. Comparison with VUV Experiment

Matsumi *et al.*¹¹ utilized VUV LIF in a cell to determine the $O(^3P_j)$ fine-structure state distribution in the quenching of $O(^1D)$ in collisions with several atomic and molecular collision partners. In their experiment, $O(^1D)$ atoms were prepared by 193 nm photolysis of N_2O , and the state distributions were determined by extrapolation to zero delay between the photolysis and probe lasers. For quenching by Kr, they estimated the nascent state branching ratios to be $j = 0/j = 2 = 0.33 \pm 0.05$ and $j = 1/j = 2$ equal 0.45 ± 0.07 at an estimated nascent average collision energy of $14.7 \text{ kcal mol}^{-1}$, or 5141 cm^{-1} . For this collision energy, we compute the following branching ratios: 1.126 for $j = 0/j = 2$ and 0.073 for $j = 1/j = 2$. There is hence significant disagreement between the experimentally measured and computed state branching ratios. We have no explanation for this disagreement. On the experimental side, perhaps there was more collisional relaxation of the nascent state distribution than anticipated. Also, the relative detection efficiency for each of the fine-structure levels must be determined; this was carried by interrogating a thermalized sample of 3P_j levels.

3. Rate Constants

We have employed the collision energy dependent cross sections for quenching of $O(^1D)$ to the sum over all the $O(^3P_j)$ fine-structure levels to determine the rate constants for O–Rg, where Rg = Ar, Kr, and Xe. The relationship between the quenching cross sections $\sigma_{O(^1D)-Rg}$ and rate constants $k_{O(^1D)-Rg}$ is³⁶

$$k_{O(^1D)-Rg}(T) = \left[\frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \int_0^\infty E_c \sigma_{O(^1D)-Rg}(E_c) e^{-E_c/k_B T} dE_c \quad (13)$$

where E_c is the collision energy and k_B is the Boltzmann constant. The upper range of integration was taken to be $E_c = 5000 \text{ cm}^{-1}$.

Figure 3 presents a comparison of our computed $O(^1D)$ –Kr quenching rate constant with the experimental measurements of this rate constant, including the present measurements reported in Sec. II B. Our computed rate constant is significantly lower than the experimental measurements. However, the calculation does satisfactorily describe the temperature dependence of the experimental data.

We compare in Fig. 11 experimental and our computed rate constants for $O(^1D)$ quenching by Ar and Xe. In contrast to the comparison of experimental and computed $O(^1D)$ –Kr quenching

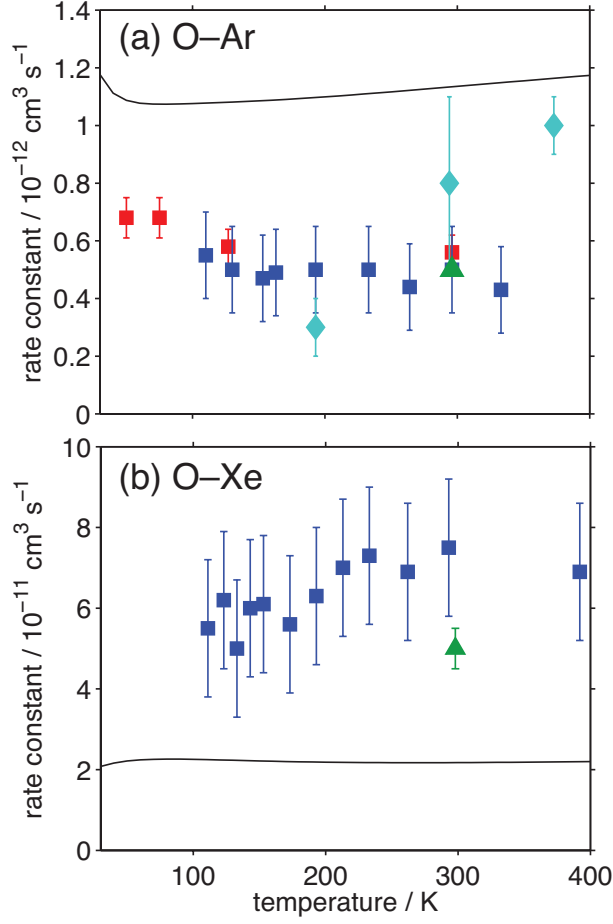


FIG. 11. Experimentally measured and computed rate constants for the quenching of $O(^1D)$ by (a) Ar and (b) Xe. Experimental values in panel (a): Red squares, Grondin *et al.* (Ref. 5); blue squares, Davidson *et al.* (Ref. 2); green triangle, Shi and Barker, upper limit (Ref. 3); cyan diamonds, Blitz *et al.* (Ref. 4). Experimental values in panel (b): Blue squares, Davidson *et al.* (Ref. 2); green triangle, Shi and Barker (Ref. 3). Computed values: black lines, this work.

rate constants, our computed rate constants for quenching by Ar are somewhat larger than the experimental values. Our calculations predict that the $O(^1D)$ –Ar quenching rate constants should increase slightly over the 10 – 300 K temperature range, while the experimental measurements show a slight decrease with increasing temperature. As can be seen in Fig. 11(b), our computed $O(^1D)$ –Xe rate constant is lower than the corresponding experimental determinations. We do see that theory and experiment both show an approximately constant rate constant as a function of temperature.

IV. DISCUSSION

The experimental rate constants obtained in this work for $O(^1D)$ electronic quenching by Kr extend the currently available experimental data for this process down to 50 K. The values are in excellent agreement with those obtained during the earlier study of Davidson *et al.*² in the 113–296 K range. In their cryogenically cooled experiments, Davidson *et al.* employed pulse laser photolysis (PLP) of O_3 at 266 nm as the $O(^1D)$ source, coupled with detection of the weak spin-forbidden $O(^1D) \rightarrow O(^3P)$ emission at 630 nm to follow the reaction kinetics. Good agreement is also obtained with the room temperature rate constant measured by Blitz *et al.*⁴ who used PLP of N_2O at 266 nm as the $O(^1D)$ source in their experiments and a chemical tracer method (through OH detection at 310 nm) to follow the progress of the quenching. By contrast, the rates obtained by Blitz *et al.* at lower temperature (195 K) are approximately 40% larger than the present values and those of Davidson *et al.* The rate constant measured by Shi and Barker³ at room temperature is lower than the values of all three other experimental studies and is also outside the combined error bars. These authors used a relative rate method to derive deactivation rate constants for a range of colliders, producing $O(^1D)$ atoms through PLP of O_3 at 308 nm.

In terms of the overall temperature dependence of the $O(^1D)$ –Kr quenching rate constant, we observe only small variations of the rate constant over the 50–296 K temperature range; a similar conclusion to the earlier work of Davidson *et al.* Indeed, the very slight positive temperature dependence we measure is well within the error bars of the experiments themselves, so the rate constants for this process are effectively temperature independent.

We compared the measured and computed rate constants for the quenching of $O(^1D)$ by Ar, Kr, and Xe in Sec. III C 3. We found that quantitative agreement was only modest. The calculations do reproduce the measured temperature dependences of the rate constants, to within the experimental errors.

Both experiment and theory display the trend of increasing magnitude of the quenching rate constants as one goes down the periodic table from Ar, to Kr, and then Xe. Two general trends were found in the potentials and spin-orbit matrix elements. Firstly, the depth of the well for the $^1\Sigma^+$ state, which derives from the $O(^1D) + Rg$ asymptotic limit increases significantly as we go down the periodic table. More importantly, the magnitude of the spin-orbit matrix elements, in particular the coupling between the $^1\Sigma^+$ state and the $\Omega = 0^+$ component of the $^3\Pi$ state, at the crossing radius increases substantially as we go down the periodic table. Similarly, the rate

constant for quenching of $S(^1D)$ by Ar (Ref. 8) is approximately an order of magnitude larger than the rate constant for $O(^1D)$ quenching by Ar. This again reflects the larger size of the spin-orbit coupling in the heavier S atom.

We do find an interesting structure to the computed quenching cross sections, which is unfortunately currently not amenable to experimental observation. The energy-dependent quenching cross sections for all three collision pairs, especially $O(^1D)$ –Kr and $O(^1D)$ –Ar, show many sharp resonance peaks due to quasi-bound levels trapped by the centrifugal barrier for the highest partial wave for which quenching occurs. These resonances, which occur for only one partial wave at a given collision energy, are a consequence of the relatively large reduced mass of these collision pairs.

V. SUPPLEMENTARY MATERIAL

See the supplementary material for the file `PES.tar`, which contains tables of the $O(^1D, ^3P)$ –Ar, Kr interaction energies and spin-orbit matrix elements of the internuclear separation R .

VI. ACKNOWLEDGMENTS

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