A new potential energy surface for OH(A $^2\Sigma^+$)–Kr: the van der Waals complex and inelastic scattering

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New *ab initio* studies of the OH(A$^2\Sigma^+$)–Kr system reveal significantly deeper potential energy wells than previously believed, particularly for the linear configuration in which Kr is bound to the oxygen atom side of OH(A$^2\Sigma^+$). In spite of this difference with previous work, bound state calculations based on a new RCCSD(T) potential energy surface (PES) yield an energy level structure in reasonable accord with previous studies. However, the new calculations suggest the need for a reassignment of the vibrational levels of the electronically excited complex. Quantum mechanical (QM) and quasi-classical trajectory (QCT) scattering calculations are also performed on the new potential energy surface. New experimental measurements of rotational inelastic scattering cross sections are reported, obtained using Zeeman quantum beat spectroscopy. The values of the rotational energy transfer cross sections measured experimentally are in good agreement with those derived from the dynamical calculations on the new adiabatic potential energy surface.

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I. INTRODUCTION

The interactions of the OH radical with noble gas atoms have been of considerable interest for many years, and the subject of numerous experimental and theoretical investigations.[1] As with the NO radical,[2] OH is an important participant in atmospheric and flame chemistry and can thus serve as a paradigm for the study of inelastic collisions of open shell species.[3] The body of experimental data available for collisions of both OH and NO provides a benchmark for theoretical calculations. These calculations can then facilitate the interpretation of experiment.

We report here a new *ab initio* adiabatic potential energy surface (PES) for the OH($A^2\Sigma^+$)–Kr system. The interaction between Kr and OH in its electronically excited state is much more attractive than that between Kr and OH in its electronic ground state, OH($X^2\Pi$).[4,5] Furthermore, the interaction of OH(A) with the polarizable Kr atom is significantly stronger than with the lighter noble gases, and as with the lighter species considerable work has been undertaken to observe and characterize the van der Waals complex spectroscopically.[4–7]

In contrast to the interactions of OH with the lighter noble gases, there have been limited theoretical studies of OH with Kr. A PES for OH(A)-Kr has been published previously by Carter *et al.*.[4,5] This was based on experimental spectroscopic measurements of the van der Waals complex. Because of unfavorable Franck-Condon factors, experiment gives little information on the excited state complex in the region of the HOKr minimum. Recently, Sumiyoshi *et al.*[8] used a combination of experimental observations and *ab initio* calculations to produce PESs for OH(X)–Kr. The effect of the OH(X) vibration was included in that study. Here, we present a high-quality, fully *ab initio* potential energy surface for the interaction of Kr with OH(A). In addition, we report, for the first time, quasi-classical trajectory (QCT) and quantum mechanical (QM) simulations of the rotationally inelastic scattering of OH(A) by Kr.

As with the spectroscopy of the complexes, there have been relatively few experimental and theoretical studies of elastic and inelastic scattering in the heavier OH(A)–rare gas (Rg) systems. However there has been considerable interest in rotational energy transfer (RET) and collisional depolarization in collisions of OH(A) with the lighter rare gases, He[9] and Ar.[9–13] Studies of OH(A) with Kr are useful in elucidating the role played by dynamical and kinematic effects in the elastic and inelastic scattering of these systems. As will be seen in

the following article, OH(A)–Kr is also of particular interest in that it is the lightest of the OH(A)–Rg systems for which collisional electronic quenching,[14] which leads to transfer of population from OH(A) to OH(X), is competitive with RET and collisional depolarization.

This paper is organized as follows. In section II the details of the calculation of the new OH(A$^2\Sigma^+$)–Kr PES are given, and its key features explored. Bound state calculations are presented in section III, and compared with previous work. The experimental and theoretical methods employed for determining the rotational energy transfer (RET) cross sections will be described in section IV, before the results are compared and discussed. The final section summarizes our main conclusions. In a forthcoming paper the same experimental and theoretical methodology employed here will be used to explore the elastic and inelastic collisional depolarization of OH(A) by Kr.

II. *AB INITIO* POTENTIAL ENERGY SURFACE CALCULATIONS

The A $^2\Sigma^+$ electronic state of OH lies $32684\,\mathrm{cm}^{-1}$ $(4.06\,\mathrm{eV})$ above the ground X $^2\Pi$ state.[15] The electron occupancy in A state can be described well as a singly-occupied bonding 3σ and doubly-occupied non-bonding $1\pi_x$ and $1\pi_y$ molecular orbitals (these are the $2p_x$ and $2p_y$ atomic orbitals on the O atom). By contrast, the ground (X $^2\Pi$) electronic state corresponds to a doubly-occupied 3σ orbital with single occupancy in either the $1\pi_x$ or $1\pi_y$ orbitals.

Because the A$^2\Sigma^+$ state is electronically non-degenerate, interaction with a noble gas atom gives rise to a single PES. Electronic structure calculations of the OH(A)–Kr(^{1}S) PES were performed with the MOLPRO 2006.2 package.[16] Following the Boys and Bernardi prescription,[17] to correct for basis set superposition error we determined the interaction energy as the difference between the total energy of the complex – the OH(A)–Kr supermolecule – and the sum of the energies of the OH(A) and Kr fragments calculated in the same supermolecular basis, namely

$$E_{\mathrm{int}} = E_{\mathrm{Kr-OH}}(R,\gamma) - E_{\mathrm{Kr}}(R,\gamma) - E_{\mathrm{OH}}(R,\gamma)\,. \tag{1}$$

A. *Ab initio* calculations

The *ab initio* calculations were performed using a standard two-dimensional grid in Jacobi coordinates, consisting of R, the distance between Kr and the center-of-mass of the OH

molecule, and γ, the angle between $\boldsymbol{R}$ and the OH bond axis $\boldsymbol{r}$. The magnitude of the latter was fixed at its equilibrium value in the A state of $r_e = 1.9126\,a_0$.[15] We define $\gamma = 0°$ to correspond to the OHKr collinear arrangement. Test calculations showed little difference in the calculated interaction energy if r were instead fixed at its average value in the $v = 0$ level of OH(A), namely $r_0 \simeq 1.95\,a_0$. The radial grid consisted of 30 points extending from $2.5\,a_0$ (high on the repulsive wall) to $26.0\,a_0$ (beyond the van der Waals region). The angular grid consisted of points placed every $20°$ with an additional point at $\gamma = 90°$.

In the electronic structure calculations we used the augmented correlation-consistent quadruple zeta (AVQZ) atomic orbital basis set of Dunning *et al.*[18,19] This basis was further augmented with a set of $3s3p2d2f1g$ bond functions[20] placed at the midpoint of $\boldsymbol{R}$ with exponents (sp) 0.9, 0.3, 0.1, (df) 0.6, 0.2 and (g) 0.3. The scalar relativistic effects were included by employing the all-electron Douglas-Kroll Hamiltonian for the Kr atom, as implemented in MOLPRO.

With this choice of basis set and grid we carried out complete active space self-consistent field (CASSCF) calculations with 5 electrons in 3 active orbitals $(3\sigma,\ 1\pi_x$ and $1\pi_y)$. From the CASSCF natural orbitals, we obtained canonical orbitals by separate diagonalization of the Fock matrix for occupied and virtual orbitals. For a given OH–Kr geometry, we used these canonical orbitals to initiate restricted Hartree-Fock (RHF) calculations for the excited $A\,^2\Sigma^+$ state or the ground electronic state (at the same geometry). The initial CASSCF calculations were utilized to ensure the proper symmetry and electron occupancy.

Starting with the RHF wavefunctions for the A and X states, we performed partially spin-restricted, coupled-cluster calculations with single, double and non-iterative triple excitations [RCCSD(T)].[21,22] By the inclusion of triple excitations and the introduction of mid-bond functions, we expect that the present *ab initio* calculations will recover a significant fraction of the correlation energy, and, hence, provide better description of the dispersion interaction than would be obtained from, for example, CASSCF calculations followed by an internally-contracted, multi-reference configuration-interaction method. An optimal recovery of the correlation energy will be particularly important for approach of the Kr to the O-end of the OH molecule.

B.   Features of the potential energy surface

The upper panel of Fig. 1 shows a contour plot of the RCCSD(T) PES for the OH(A $^2\Sigma^+$)–Kr van der Waals complex, plotted as a function of the two Cartesian components of $\boldsymbol{R}$. The lower panel of the figure presents a similar contour plot of the RCCSD(T) PES for the OH(X $^2\Pi$)–Kr ground state. The excited state PES is highly anisotropic compared with that of the ground state, and possesses very two deep minima at both colinear geometries: OHKr ($\gamma = 0°$) and HOKr ($\gamma = 180°$). These minima are separated by a saddle point in T-shaped geometry.

The parameters of the global and local minima for the OH(A)–Kr PES are listed in Table I (the zero of energy corresponds to OH(A,r_e)+Kr at $R = \infty$). The depth of the global minimum ($R = 4.01\,a_0$, $\gamma = 180°$) is $\sim 6079\,\text{cm}^{-1}$ (0.76 eV). The secondary OHKr minimum ($\gamma = 0°$) is located at $R = 5.4\,a_0$, with a well depth of $\sim 1949\,\text{cm}^{-1}$ (0.24 eV). As one can see in Fig. 1, the saddle point corresponds to an energy of less than $-80\,\text{cm}^{-1}$ at approximately $R = 7.5\,a_0$, only slightly below the OH(A) + Kr dissociation asymptote. Thus, there is a substantial barrier ($\gtrsim 1850\,\text{cm}^{-1}$) to interconversion between the OHKr and HOKr minima. The OH(A $^2\Sigma^+$)–Kr system can therefore be thought of as existing as two conformers, Kr–HO(A) or Kr–OH(A), with the latter being the lowest energy geometry.

As can be seen in Table I, the position of the KrHO minimum is close to the predictions of the earlier empirical PES of Carter et $al.$[4] This PES was adjusted to obtain a best fit to the experimentally available data on the OH(A←X) electronic transitions in the complex.[4] Our well depth for the KrHO minimum is $469\,\text{cm}^{-1}$ shallower than predicted by the semi-empirical PES of Carter et $al.$. Treating the OH(A) as rigid, we predict a zero-point corrected dissociation energy for the KrHO isomer of $1357\,\text{cm}^{-1}$, in agreement with the experimental lower limit estimate of $1131\,\text{cm}^{-1}$ of Lemire et $al.$, which applies, since it is based on electronic spectroscopy of the OH(X)–Kr complex, to the OH(A)–Kr minimum.

We have found the collinear HO(A)Kr minimum to be more than a factor of three deeper than the OH(A)Kr one. Because of the lack of experimental information probing the KrOH(A) well, Carter et $al.$ kept the position and depth of the KrOH(A) minimum arbitrarily fixed during the optimization procedure. Therefore we cannot compare the two PESs quantitatively in this region. The zero-point corrected dissociation energy of the HO(A)Kr isomer is $4341\,\text{cm}^{-1}$ (0.54 eV). As has been discussed by Ho et $al.$,[23] and in our

earlier work on the Ar–OH(A) system,[24] because of the poor Franck-Condon overlap between the lowest ro-vibronic state of the OH(X)Kr complex and the bend-stretch states of the HO(A)–Kr complex, the electronic spectroscopy of the OH–Kr complex cannot probe bend-stretch states lying near the HO(A)–Kr minimum. Thus empirically-adjusted PES's cannot provide a reliable prediction of the strength of the van der Waals interactions in this region.

More detailed comparison of the Kr–OH(A) PES with the A′ and A″ Kr–OH(X) PESs reveals that the latter two PESs are considerably more repulsive at $\gamma = 180°$ (corresponding to KrOH). This is illustrated in Fig. 1, which compares the ^{2}A′ Kr–OH(A) and ^{2}A′ Kr–OH(X) PESs. In particular, the position of the OH(A)Kr minimum corresponds to a point high on the repulsive wall of the OH(X)Kr PES. However, the OHKr well on the OH(A)Kr PES can easily be accessible by electronic excitation of the OH(X)–Kr complex in the region of its minimum ($R \approx 7.2\,a_0$, $\gamma = 0°$). Consequently, the observed electronic spectroscopy of the OH–Kr complex corresponds exclusively to excitation of higher bend-stretch states of the OH(A)–Kr complex. Note, that because the OH(A)–Kr minimum lies at a far smaller value of R than the minimum on the OH(X)–Kr PES, only OH(A)–Kr stretch levels with $v > 3$ were experimentally accessible.[4]

Fig. 2 compares the electronically excited PES determined here for OH(A $^2\Sigma^+$)–Kr with those obtained previously using similar theoretical techniques for OH(A $^2\Sigma^+$)–Ar.[10] The two systems display many common features, such as the minima at the colinear configurations, and the significant barriers to interconversion between the two linear isomers. However, the OH(A $^2\Sigma^+$)–Kr system is more anisotropic, and the HOKr and OHKr well depths differ significantly. Likely, these differences in the OH(A)Ar and OH(A)Kr PES's will lead to a qualitatively different spectrum of van der Waals level and different scattering dynamics.

III. BOUND STATE CALCULATIONS

A. Glossary

The rotational/fine-structure levels of the free OH(A$^2\Sigma^+$) radical are shown in Fig. 3. In the remainder of this paper we employ the following notation: N denotes the OH nuclear rotational angular momentum apart from electron and nuclear spin. For OH(A$^2\Sigma^+$), which

has zero electronic orbital angular momentum, N is equivalent to the nuclear rotational angular momentum, which must lie perpendicular to the internuclear axis, r. Consequently, the body-frame projection of N, which we designate M_N, is zero. The total OH($A^2\Sigma^+$) rotational angular momentum apart from nuclear nuclear spin is designated j. In the Hund's case (b) coupling scheme appropriate for OH($A^2\Sigma^+$), for which the electron spin $S = 1/2$, each rotational level N exists as two closely-spaced spin-rotation (SR) doublets with $j = N \pm 1/2$, except for $N = 0$, where only $j = 1/2$ is allowed. These levels are split by the spin-rotation coupling Hamiltonian

$$\hat{H}_{\text{sr}} = \gamma_{\text{sr}} N \cdot S \,, \tag{2}$$

where γ_{sr} is the spin-rotation coupling constant, so that the splitting between the two spin-rotation levels is

$$\Delta E_{\text{sr}} = (2N + 1)\, \gamma_{\text{sr}} \,. \tag{3}$$

The levels with $J = N + 1/2$ and $J = N - 1/2$ are designated as F_1 and F_2, respectively.[25]

The total angular momentum quantum number of the Kr + OH(A) system is denoted J with projections M_J along the space-fixed Z axis and P along the body-frame axis, which is taken to be the Jacobi vector R.

B. Bound states of the complex

Bound states of the Kr–OH($A^2\Sigma^+$) complex based on our new PES were calculated using the full quantum close-coupling (CC) method, the computationally simpler coupled-states (CS) approximation[26,27] and the even more simplified adiabatic bender (AB) approximation.[28,29] We also used a collocation method[30–32] within a spin-free approximation, *i.e.* treating OH(A) as a closed shell molecule. We have also performed one-dimensional (1-D) discrete variable representation (sine-DVR) calculations[33] of the vibrational bound states with the potential restricted to $\gamma = 0°$. Below we will discuss details and results of the 2-D and 1-D DVR dynamics.

For the CC and CS calculations we used the Hibridon package[34] for total angular momentum $J = 1/2$. The radial part of the wave functions in these bound states calculations is represented by 213 Gaussian functions, equally distributed basis between $R = 3.4$ and

$14\,a_0$.[30] The molecular parameters for $OH(A^2\Sigma^+)$ employed in the calculations were the reduced mass of $14.1380\,u$, the rotational and centrifugal distortion constants for the $v = 0$ vibrational state ($B_0 = 16.9602\,cm^{-1}$, $D_0 = 2.039 \times 10^{-3}\,cm^{-1}$, $H_0 = 8.71 \times 10^{-8}\,cm^{-1}$) and the spin-rotation coupling constant of $\gamma_{sr} = 0.201\,cm^{-1}$.[15,35] Converged bound states were obtained with a rotational basis of OH(A) extending up to $j = 27.5$, with a grand total of 11715 radial-angular functions.

In the adiabatic bender (AB) approximation[28,29] the total Hamiltonian, exclusive of the R-dependence of the OH–Kr relative motion and the rotational motion of the OHKr system, is diagonalized as a function of R. The eigenvalues define a set of AB potentials on which 1-D DVR calculations of the vibrational states can be performed. For weakly-bound complexes, the one-dimensional vibrational eigenvalues in these potentials provide an excellent approximation to the bend-stretch levels. Often, the centrifugal-decoupling approximation[26,27] is also invoked, within which the AB potentials and eigenvalues are also labelled by P, the projection of the total angular momentum along R. Fig. 4 shows the lowest three AB potentials for $P = 1/2$. The potentials for $P = 3/2$ have much shallower wells. The three $n = 1$, 4 and 5 AB potentials shown correlate, asymptotically, with the lowest three rotational states of OH(A): $N = 0\,(J = 1/2)$, $N = 1\,(J = 3/2)$ and $N = 1\,(J = 1/2)$. In the following we will label the states by n (the cardinal number of the adiabatic bender potential) and v_s the stretching quantum number within the particular AB potential. The $n = 2$ and $n = 3$ AB curves not shown in Fig. 4 are also localized near HO–Kr collinear geometry similarly to the $n = 1$ curve and asymptotically correlate to $N = 2$ and $N = 3$ rotational states, respectively. The vibrational energy levels associated with the displayed AB potentials are also indicated in the figure. The $n = 4$ and $n = 5$ AB curves are localized predominantly near collinear OH–Kr geometry ($\gamma = 180°$).

The energies and vibrationally averaged rotational constants of the OH(A)–Kr complex calculated on the new PES using a 2-D treatment of the dynamics are shown in Table II, together with relevant experimental results.[4] The rotational constants were obtained by averaging the $\frac{1}{R^2}$ term using wave functions corresponding to a given bound state and, similarly, the average angle, $\bar{\gamma}$, was obtained from average value of the $\cos(\gamma)$. For each state we also list the average value of the Jacobi angle γ, which provides an indication of the region of configuration space where the bound state is located. Also, all bound state energies for van der Waals stretching quantum numbers $v_s > 5$ are shown relative to the

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$v_s = 5$ energy level.

The vibrational energy levels and rotational constants calculated using 1-D sine-DVR with a potential cut at $\gamma = 0°$ are given in Table III similarly for $v_s > 5$ and relative to $v_s = 5$ energy level. Interestingly, one can notice that the agreement with the experiment is much better for both the energies and rotational constants than with full 2D calculations. This could stem from the fact that the experiment is only sensitive to the KrHO minimum or that the experiments were analyzed using a 1D approach.[4] Fig. 5 displays contour plots of the $\{n = 1, v_s = 0\}$ and $\{n = 4, v_s = 0\}$ bend-stretch wavefunctions. Electronic excitation will access predominately the states corresponding to the $n = 4$ adiabatic-bender potential, and which are localized near collinear OH–Kr geometry. The Franck-Condon factors will be much smaller for the $n = 1, v_s$ states, which are localized near collinear HO–Kr geometry and also, at least for the lowest values of the stretching quantum number, located at values of R which lie considerably inside the region sampled by the lowest $OH(X)$–Kr bend-stretch state. Tables IV and V list the vibrational spectrum associated with the lowest $HO(A)$–Kr AB curve $(n = 1)$ and with the lowest $OH(A)$–Kr $(n = 4)$ curve.

The fact that the agreement with the experiment is much better for the 1D calculations than with the full 2D calculations suggests another interpretation, that either the theoretical 2D or the experimentally determined energy levels have been mis-assigned. We have carefully checked the contour plots of the wave functions, and so we believe that our 2-D theoretical assignments of the energy levels are correct. Given that the band origin was not observed experimentally, the possibility of a mis-assignment of the experimental energy levels should not be ruled out.[6] In Table VI we show a revised comparison between experiment and theory, in which the quantum number v_s is reassigned, so that the energy levels are referenced to the $v_s = 3$ level, rather than to $v_s = 5$. The agreement for the energy level spacings is much improved relative to that observed in Table II, using the original experimental assignments. The agreement for the vibrationally averaged rotational constants is also significantly improved. In Table VII we show results from the 1D sine-DVR method, but with the origin set at $v_s = 3$, rather than at $v_s = 5$ as in Table III. With the revised assignment we observe a worsening of the agreement between 1D DVR results with experiment compared with the 2D results, as expected. Clearly, these data support the view that further work on the vibrational assignments of both Kr–OH(A), and the isotopomer Kr–OD(A), which has also been observed experimentally,[4] would be valuable.

As shown in Tables IV and V, we observe almost perfect agreement between the bound-state energies obtained from the open-shell CC and CS calculations and the closed-shell collocation calculations. Although it is known that the spin-rotation coupling can be different in the complex than in the free diatomic,[36] inclusion of the small spin-rotation coupling has little effect on the position of the bend-stretch levels of the OH(A)–Kr complex. In addition, both the CS and AB energies are very close to the exact values. Because the three AB potential curves (Fig. 4) are so distinct for both collinear isomers, there is very little mixing between these AB states for most of the vibrational levels.

IV.   OH(A)–KR COLLISION DYNAMICS

A.   General considerations

As discussed originally by Corey and McCourt,[37] since the electronic Hamiltonian contains purely electrostatic terms, the spin ($S = 1/2$) acts a spectator during the interaction with Kr. The OH(A) rotational levels correspond to a parallel ($j = N + 1/2$) or antiparallel ($j = N - 1/2$) coupling of N and S (see Fig. 3). The dynamics of the collision – the effect of the electrostatic forces acting on the OH and Kr fragments – is fully contained in the probability amplitudes (S-matrix elements) for transitions between OH states of different N. The amplitudes for transition between different j states can then be obtained by vector recoupling with the spin S. Two types of process are possible: transitions in which the relative orientation of N and S is unchanged, so that $\Delta N = \Delta j$ (we shall call these spin-rotation conserving transitions) and transitions in which the relative orientation of N and S is changed from parallel to antiparallel (or vice versa). In this case $\Delta j = \Delta N \pm 1$. We shall refer to this second type of process as spin-rotation changing.

Since the collision is governed by a single PES, we might anticipate that the scattering of OH(A) with a noble gas is amenable to a careful QCT treatment, in which the nuclear rotational angular momentum of the diatomic is the important dynamical variable. The recoupling with the spectator spin can then be treated in a classical analogue of the quantum treatment, as has been recently presented.[11,13,38]

B. Quantum scattering

Fully quantum close-coupling (CC) scattering calculations of integral cross sections were performed on our new *ab initio* adiabatic Kr-OH(A$^2\Sigma$) PES using the HIBRIDON suite of programs.[34] The rotational basis included all states with $N \leq 29$. The calculations were performed at the same fixed collision energy as described below in QCT subsection IV C. Numerical propagation of the wave function extended from $R = 3\,a_0$ to $30\,a_0$. Inclusion of 300 partial waves was sufficient to ensure convergence of all inelastic cross sections.

C. QCT Method

Batches of approximately 1×10^5 trajectories were run for several initial N states at a fixed collision energy of $0.039\,\text{eV}$ $(314.6\,\text{cm}^{-1})$. This collision energy corresponds to the mean of a thermal distribution, $\langle E_c \rangle = 3/2\,k_B T$, at $300\,\text{K}$. The method employed was similar to that described in Ref. 39.

For comparison with the fixed collision energy QCT data, batches of trajectories were also run with a variable collision energy. In this case, thermally averaged cross sections were determined from the state specific thermal rate coefficients

$$k_{i \to f}(T) = \left[\frac{8}{\pi \mu (k_B T)^3} \right]^{1/2} \int_0^\infty \sigma_{i \to f}(E_c)\, E_c \exp\left(-E_c/k_B T\right) \mathrm{d}E_c\,, \tag{4}$$

by dividing by the mean relative velocity

$$\langle v_{\text{rel}}(T) \rangle = \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2}, \tag{5}$$

to give

$$\langle \sigma_{i \to f}(T) \rangle \equiv \frac{k_{i \to f}(T)}{\langle v_{\text{rel}}(T) \rangle} = \frac{1}{(k_B T)^2} \int_0^\infty \sigma_{i \to f}(E_c)\, E_c \exp\left(-E_c/k_B T\right) \mathrm{d}E_c\,. \tag{6}$$

As will be shown in section IV F 3, the thermally averaged cross sections and those calculated at a fixed collision energy corresponding to the mean at $300\,\text{K}$ were generally in excellent agreement.

Since the adiabatic potential was only calculated for OH(A$^2\Sigma^+$) at its equilibrium internuclear distance, the method of Lagrange multipliers was used to force rigid rotor behavior during the integration of the classical equations of motion. To assign the final state for each

trajectory, the square of the rotational angular momentum $|\boldsymbol{N'}|^2 = N'(N'+1)\hbar^2$ was first calculated, and then the values of N' thereby obtained were rounded to the nearest integer. Trajectories whose final N' state were found to lie between $N \pm 0.5$ were considered elastic.

At a fixed collision energy, the expression for the inelastic cross section is

$$\sigma_{N \to N'}(E_c) = \pi b_{\text{max}}^2 \frac{\mathcal{N}_{N'}}{\mathcal{N}_{\text{tot}}} , \qquad (7)$$

where $\mathcal{N}_{N'}$ is the number of trajectories ending in state N', and $\mathcal{N}_{\text{tot}}$ the total number of trajectories (elastic plus inelastic). The maximum impact parameter leading to inelastic trajectories was determined by monitoring the change in the rotational quantum number, ΔN, with the criterion that no trajectories with $|\Delta N| > 0.5$ took place for $b > b_{\text{max}}$. Equation (7) implies that the impact parameter for the i-th trajectory is sampled according to $b^{(i)} = \xi^{1/2} b_{\text{max}}$, where ξ is a random number in the interval $(0, 1)$. In the present work, b_{max} was set to $6.0\,\text{Å}$ for $N = 0$, $5.5\,\text{Å}$ for $1 \leq N < 5$ and $5.0\,\text{Å}$ for $N \geq 5$.

Note that the above treatment is appropriate for QCT calculations in which OH(A) + Kr is treated as a closed shell system. QCT estimates of the 'open shell' spin-rotation and hyperfine level changing cross sections were obtained using the tensor opacity formalism described in detail previously.[11,13,38] We focus here on the method used to calculate QCT open-shell opacity functions, since these have not been presented previously. The tensor opacities resolved in the total angular momentum quantum number, J, can be calculated using[11]

$$P_{NN'}^K(J) = k_i^2 b_{\text{max}}^2 \frac{[N]}{[J]} \frac{\mathcal{N}_{NN'}(K, J)}{\mathcal{N}_N} , \qquad (8)$$

where $[N]([J]) \equiv 2N + 1(2J + 1)$, $\mathcal{N}_{NN'}(K, J)$ is the number of trajectories going from rotational level N to N' with angular momentum transfer of K at total angular momentum J, and $\mathcal{N}_N$ is the total number of trajectories starting in level N. k_i is the initial wavevector of the collision. (Note that this expression is formally defined for $P_{NN'}^K(\ell)$, where ℓ is the orbital angular momentum (see Eq. (A16) of Ref. 11 and Ref. 40). However, since J rapidly becomes much greater than j or N, the total angular momentum, J, can loosely be identified with ℓ.) These tensor opacities are spin-independent and can be calculated from closed-shell trajectory calculations,[11] but can be used to obtain QCT open-shell state-to-state J-partial cross sections, on the assumption that electron spin is a spectator in the collision, *via* the

equation

$$\sigma_{NjN'j'}(J) = \frac{\pi}{k_i^2}[j'][J] \sum_K \begin{Bmatrix} N & N' & K \\ j' & j & S \end{Bmatrix}^2 P_{NN'}^K(J).$$ (9)

These partial cross sections can be converted into opacity functions (probabilities as a function of J) with the relation[40]

$$P_{NjN'j'}(J) = \frac{k_i^2}{\pi} \frac{[j]}{[J]} \frac{\sigma_{NjN'j'}(J)}{2\min(J,j)+1}.$$ (10)

The opacity functions presented here have been expanded as a Legendre series, as described previously.[39]

D. Experimental Methods

The experimental procedures for determining the RET cross sections from elastic depolarization measurements using Zeeman quantum beat spectroscopy (ZQBS) have been described previously,[9,12,13] and only a brief summary will be given here. Note that the elastic and inelastic depolarization cross sections will be presented in a forthcoming paper.

OH(X) was generated by pulsed 193 nm photodissociation of hydrogen peroxide.[41–49] H_2O_2 was flowed in a 50:50 mixture with water through the reaction chamber at a constant partial pressure of $\lesssim 20$ mTorr. Electronically excited OH(A) radicals in $v = 0$ were obtained at a fixed photolysis-probe laser delay of $\sim 10\,\mu$s by pulsed excitation of OH(X) using the (0-0) band of the A←X transition. The experiments were performed with Nd:YAG-pumped dye laser probe radiation (bandwidth ~ 0.36 cm^{-1} in the UV), in counter-propagating laser beam geometry. The minimum pressure of collider gas used was kept above ~ 50 mTorr, sufficient to allow translational moderation of OH(X) down to 300 K.

The collider gas, Kr, was flowed into the chamber through a separate inlet valve to allow experiments to be performed over a range of partial pressures from ~ 50 mTorr to ~ 1500 mTorr. The OH(A) spontaneous fluorescence was passed through a set of polarizing optics (see below), and the emission was then dispersed using a monochromator, before being detected with a UV-sensitive photomultiplier. With this method it is possible to monitor transitions from single rotational states allowing the contribution from RET collisions to be determined. The fluorescence decay traces were recorded on a digital oscilloscope and transferred to a PC for subsequent data acquisition and analysis. The response time of the

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system was determined to be $\lesssim 20\,$ns. A complete list of transitions employed, together with the monochromator resolutions, is given in table 1 of Ref. 9.

A Glan-Taylor polarizer was used to improve the polarization of the frequency doubled dye laser radiation immediately prior to entering the reaction chamber, and the purity of the polarization was determined to be better than 95% on exiting the chamber. In the case of linearly polarized probe measurements, a photoelastic modulator was used to switch the probe laser polarization either 90° to the fluorescence detection direction or parallel to it on alternate laser shots. The polarizer used for detection was aligned parallel to the probe laser propagation axis. The photolysis laser radiation was used without polarization. In the case of orientation measurements, the probe radiation was switched between left and right circularly polarized light on alternate laser shots using a photoelastic modulator. A quarter waveplate followed by a Glan-Taylor polarizer were placed in front of the entrance slits of the monochromator.

The ZQBS experiments were performed in a uniform magnetic field of between 0 and 50 Gauss. The field was produced using a pair of matched Helmholtz coils, which were placed inside the reaction chamber, about 2.5 cm away from the interaction region. As in our previous work,[9,12,13,50–52] the centre of the reaction chamber was screened from external magnetic fields by μ-metal shielding. The field was checked using a Hall probe, but could also be determined from the Zeeman beat frequency, since the g_F values for OH(A) are known quite precisely.[53–60] For the linearly polarized experiments, the axis of the magnetic field was aligned parallel to the fluorescence detection direction, while for the circularly polarized experiments the field was directed orthogonal to the fluorescence detection axis and the probe laser propagation axis.

E. Data analysis

Full details of the analysis of the ZQBS data has been presented previously.[9,12,13,50,51] The non-zero nuclear magnetic moment of the H-atom nucleus ($I = 1/2$) splits the rotational levels of OH($A^2\Sigma^+$) into two hyperfine components, characterized by the total angular momentum $\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{j}$. The applied magnetic field lifts the degeneracy of the magnetic sublevels of each of these hyperfine components (Zeeman splitting) resulting in $2F + 1$ components characterized by the quantum number M_F (the projection quantum number along the mag-

netic field direction). The dye laser employed in the present work has a pulse duration of ~ 5 ns, and hence quantum beats between levels split by more than ~ 30 MHz will be unobservable. The energy splitting between the two hyperfine states of OH(A) with different F quantum numbers is of the order of several hundred MHz[61,62], hence only the beats between Zeeman components of the individual hyperfine sublevels are observed in the present study.

The RET cross sections were obtained in two ways. For those experiments which used linearly polarized light, the population decay was obtained from signals recorded with the probe laser polarization switched on alternate laser shots between parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) configurations with respect to the detection polarization. The RET cross sections were obtained by fitting field-off data, using $I_{\parallel} + 2I_{\perp}$, which is only sensitive to the population decay. In the case of circularly polarized probe radiation, the summed data $I_L + I_R$ was used to obtain the RET cross sections, where I_L and I_R are the signals obtained using left and right circularly polarized light respectively. In principle, these summed signals have a very small quantum beat arising from rotational alignment, which has twice the frequency of the orientation beat. In practice, the present experiments were insufficiently sensitive to observe this quantum beat.

The RET cross sections were obtained from fitting the summed data using:

$$I = A\,\mathrm{e}^{-(k_0 + k_1[\mathrm{Kr}])t}\,. \tag{11}$$

This population decay is associated with processes that remove OH(A), such as fluorescence (k_0) or electronic quenching (k_1). Unlike our previous study on OH(A) + Ar[9], the electronic quenching rate constant is not negligible for OH(A)+Kr, and therefore k_1 is the sum of the RET rate constant of interest and the electronic quenching rate constant. However, the rate of electronic quenching can be found by fitting the undispersed fluorescence measurements in the same way as those where the emission is recorded from just a single state. The thermal averaged electronic quenching cross-sections, $\langle \sigma_{\mathrm{EQ}} \rangle = k_{\mathrm{EQ}}(T)/\langle v_{\mathrm{rel}} \rangle$, obtained are compared with those from a previous study by Hemming *et al.*[14] in Fig. 6, in which the two sets of data are shown to be in excellent agreement.

For each rovibronic transition, a series of between 6 and 8 fluorescence decay curves obtained as a function of collider concentration were fitted globally, using the signal amplitudes, A, and the two rate coefficients as adjustable parameters. Errors were estimated using a Monte Carlo error routine described elsewhere.[63] Typical fluorescence data are shown in

Fig. 7.

F.   Dynamics: results and discussion

1.   QM vs QCT

Fig. 8 presents a comparison between the open-shell opacity functions for the OH(A)–Kr system predicted by the QM and QCT calculations. We exclude purely elastic ($N' = N$ $j' = j$) transitions for which the opacity function cannot be obtained from a QCT method. The left panels refer to collisions in which the relative orientation of $\boldsymbol{N}$ and $\boldsymbol{S}$ is conserved, so that $\Delta j = \Delta N$. The middle panels, labelled 'inelastic SR changing', show collisions in which both the rotational level N and the relative orientation of $\boldsymbol{N}$ and $\boldsymbol{S}$ change, so that $\Delta j = \Delta N + 1$, while the right panels shows the 'pure' SR-changing case for which $N' = N$ with $j' = j + 1$.

For all N levels considered, good agreement is seen between the CC QM and QCT data. The oscillations in the CC QM opacity functions arise from the existence of quasi-bound states associated with the deep, constricted wells in the PES, and are, as one might anticipate, not observed in the QCT calculations. For higher initial rotational states, N, the energy level spacing increases, and therefore inelastic SR-conserving and changing collisions – which involve a change in N – becomes less likely, particularly at higher impact parameters (larger partial waves). This is evident in the left and middle columns of Fig. 8. However, pure SR-changing collision, which conserve N, display very similar opacity functions irrespective of the value of N (right panels of Fig. 8). For these collisions, the range of impact parameters decreases only very slightly with increasing initial rotational state. Since electron spin is a spectator to the dynamics,[11] pure spin-rotation level changing collisions must arise from collisions which reorient the rotational angular momentum, $\boldsymbol{N}$. Fig. 8 shows this type of reorientation is still important for OH(A)–Kr even at high N and high J.

The fact that pure spin-rotation changing collisions remain important over a wide range of N indicates that elastic depolarization will also be important in OH(A) + Kr up to relatively high rotational states.[9,13] Pure spin-rotation changing collisions preferentially sample large impact parameters, which correspond to the relatively long range regions of the OH(A)–Kr PES shown in Figs. 1 and 2. These long-range attractive collisions remain effective in

N-conserving, reorienting transitions, irrespective of the degree of rotation of the OH(A) molecule.

A comparison of the open-shell RET cross sections from the QM and QCT calculations is presented in Fig. 9. The left- and right-hand columns display, respectively, the spin-rotation conserving and spin-rotation changing cross sections. The initially populated spin-rotation level is the F_2 level ($j = N - 1/2$) with N=2 (top), N=5 (middle) and N=8 (bottom). For both spin-rotation level conserving and spin-rotation level changing transitions, the agreement between QM and QCT at all N is excellent.

As N increases, collisions which only change the spin-rotation level become more significant, as the increasing energy transfer required to bring about a change in N becomes less favoured. This is also seen in Fig. 10, where the total height of the bars represents the total RET cross sections summed over all final N', j' states. The top (white) section of the bars corresponds to pure spin-rotation state changing (ΔN=0, $|\Delta j| = 1$) cross sections from the QCT calculations. The height of the middle section of the bar (blue) corresponds to transitions with $\Delta j = \Delta N \pm 1$ and $\Delta N \neq 0$, whereas the height of the bottom sections of the bars (red) correspond to transitions where $\Delta N = \Delta j \neq 0$. For N=0, there is only a single spin-rotation level corresponding to j=1/2, and therefore there is no pure spin-rotation state changing inelastic contribution. The right hand panel is for the initial F_2 ($j = N - 1/2$) spin-rotation level. The purely spin-rotation changing cross sections ($\Delta N = 0, \Delta j = +1$) are larger than those for initial F_1 states and are approximately constant with N. For transitions starting in both F_1 and F_2 spin-rotation levels, the contribution of spin-rotation changing collisions play a more dominant role in energy transfer with increasing N as RET with $\Delta N \neq 0$ becomes less efficient.

The contributions to the total RET cross sections from the QM calculations are also presented in Fig. 10 as open symbols. As in the previous figure, there is good agreement between the QM and QCT results, particularly at higher N. At lower N, there are small discrepancies between the two sets of data. This seems to be mainly due to the different contributions made by transitions which change both N and the relative orientation of $\boldsymbol{N}$ and $\boldsymbol{S}$ (represented by the blue section of the bar in the case of the QCT calculations, and the difference between the red squares and blue circles in the case of the QM calculations). The discrepancy at low N may reflect errors introduced by the arbitrary angular momentum binning in the QCT calculations and the repercussions of this on the recoupling of $\boldsymbol{N}$ and

S.

Pure spin-rotation changing collisions (the white bars in Fig. 10) clearly play an important role in OH(A) + Kr over a wide range of initial rotational states. As noted above, given that spin is treated as a spectator in the dynamical calculations, a change in spin-rotation state requires a significant change in the direction of $\boldsymbol{N}$. The data presented in Fig. 10 therefore suggest that angular momentum depolarization plays an important role in the OH(A) + Kr system. We will investigate this aspect of the scattering of OH(A) by Kr more fully in a forthcoming paper.

2. Comparison with OH(A) + Ar

The data shown for OH(A)–Kr in Figs. 8 to 10 can be compared with those for OH(A)–Ar published previously.[9,10,12,13] Overall, the data for OH(A)–Kr are strikingly similar to the analogous results for OH(A)–Ar. The opacity functions show similar trends with initial j, and display significant elastic and inelastic scattering probabilities over similar ranges of total J, or impact parameter, b. Pure spin-rotation changing ($\Delta N = 0$) collisions have higher cross sections for OH(A)–Kr than for OH(A)–Ar, particularly at high N, but the cross sections for inelastic, N-changing collisions are very similar in magnitude for the two systems. As we have noted above, the pure spin-rotation changing collisions require a significant changing in the relative orientation of $\boldsymbol{N}$ with respect to $\boldsymbol{S}$, and take place preferentially at long range. The differences in pure spin-rotation changing cross sections for the two systems therefore are likely to reflect differences in the long range portions of the PESs shown in Fig. 2. Note that the attractive limb of the OH(A)–Kr PES extends to longer range than that for OH(A)–Ar.

The similarity in the RET (N-changing) cross sections for OH(A) in collision with Ar and Kr is likely to reflect a number of factors. The kinematics of the two systems are quite similar, so that mass effects are unlikely to lead to large differences between the two systems. Furthermore, it might be expected that collisions which induce RET are more likely to sample the H-end of the OH(A) molecule, where the OH(A)–Kr and OH(A)–Ar PESs are more similar. This will lead to a greater similarity in the RET cross sections than might be expected based on inspection of the full PESs. We note, however, that while there is a modest preference for RET collisions favouring the H-atom end of the molecule,

at low N classical trajectories are found to sample both of potential energy wells with near equal probability,and are not confined to the long range portion of the PES. Given that the well depths in both systems are significantly larger in magnitude than the collision energies sampled at 300 K, it seems reasonable that RET cross sections are little influenced by the precise depth of the interaction potential.

3. Experiment compared with theory

Most of the dynamical calculations presented here were performed at a fixed collision energy of 0.039 eV, whereas the experimentally measured quantities are thermal rate constants. In Fig. 11 we compare QCT cross sections obtained at fixed collision energy with those obtained from the rigorous thermal averaging over the Maxwell-Boltzmann distribution, as given by Eq. (6). The excellent agreement between the two data sets shown in the figure demonstrates that the fixed energy calculations provide an excellent estimate of the true thermally averaged cross sections.

Fluorescence decays derived from the sum of those recorded with left and right circularly (or orthogonal linearly) polarized probe radiation were fit to obtain the thermally averaged RET cross sections. These were obtained by dividing the experimentally determined rate constants by the average relative velocity at 300 K. These are presented in Fig. 12 and Table VIII, alongside the results from the QCT and QM calculations determined at a fixed collision energy of 0.039 eV. The left- and right-hand panels of the figure show, respectively, the RET cross sections for transitions out of F_1 as compared to F_2 spin-rotation levels.

The theoretical thermally-averaged RET cross sections are also in good agreement with the experimentally determined values, although slightly larger at low N. As in our previous study of collisions of OH(A) with Ar,[9] only the first 100–200 ns of the fluorescence decays were used in the analysis to avoid including the effects of secondary collisions which can repopulate the initially populated spin-rotation level. This population back transfer is likely to be more significant at low N, and could be responsible for the small discrepancy between the experimental and theoretical values. However, it was found that the analysis was relatively insensitive to the timescale over which the decays were fit.

Overall, the level of agreement between the experimental and theoretical rotational energy transfer cross sections is encouraging, and suggests that the adiabatic PES developed

here is sufficiently accurate for dynamical calculations. Given the relative importance of electronic quenching at low N it is somewhat surprising that the dynamical calculations are able to reproduce the experimental RET cross sections without the need to include the electronic quenching channel. It will be of interest to see whether such calculations are able to reproduce other aspects of the collision dynamics. These matters will be explored further in a forthcoming paper, in which collisional depolarization of NO(A) and OH(A) with Kr are compared in detail.

V. CONCLUSIONS

We have reported a new *ab initio* potential energy surface OH($A^2\Sigma^+$)–Kr system, in which the OH was held at its equilibrium distance. The present *ab initio* calculations predict a significantly deeper potential energy wells that anticipated in earlier PESs, particularly for the linear configuration in which Kr approaches the oxygen atom end of OH.[4,5] The two linear OH(A)–Kr and HO(A)–Kr conformers are separated by a considerable barrier, with the Kr–O–H configuration having a well depth in excess of $6000\,\mathrm{cm}^{-1}$. In spite of the significant difference between our PES and those developed previously, the calculated bound states corresponding to the OHKr conformer are in reasonable accord with previous work.[4,5] This is certainly a reflection of the fact that the Franck-Condon region accessed by the X→ A transition used to characterize the complex spectroscopically, on which the prior PESs are based, is localized nearly exclusively in OHKr geometry. The new calculations suggest a revised assignment of the vibrational levels of the stretching mode of the complex, which is shown to lead to a significant improvement in the agreement between experiment and theory.

It is clear from these results, as well as our previous discussion of the OH(A)–Ar complex,[24] that there exists an intriguing deep well on the excited OH(A)–noble gas PESs which is so far experimentally inaccessible. We urge further exploration of this feature.

Quantum mechanical and quasi-classical trajectory scattering calculations were performed on the new adiabatic PES. The QM and QCT cross sections generally agree well. This good agreement between o-s QM and QCT is due to the fact that the collision of OH in its $A^2\Sigma^+$ state can be described by a single PES with the spin acting solely as a spectator. The calculated rotational energy transfer cross sections are also in excellent agreement

with values obtained experimentally by means of Zeeman quantum beat spectroscopy. The experiments also yield electronic quenching cross sections for OH(A) + Kr, which are in good accord with the results of previous studies.[14] In contrast to the inelastic collisions of OH(A) with the lighter noble gases He and Ar,[10] electronic quenching to the ground $X^2\Pi$ state is important for OH(A) + Kr. A full characterization of this process will require a treatment of non-adiabatic (electronically inelastic) scattering, an investigation of which is now underway.

ACKNOWLEDGMENTS

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PES	R	D_e	D_0
	KrHO minimum		
RCCSD(T)[b]	5.40	1949	1357
Carter's PES[c]	5.24	2418	1772
	KrOH minimum		
RCCSD(T)[b]	4.01	6079	4341
Carter's PES[c]	4.16	1900	. . .

TABLE I. Characterization of global and local minima on the Kr–OH(A$^2\Sigma^+$, $r = r_\mathrm{e}$) PES and comparison with PES of Carter *et al.*[4].[a] We note that the comparison of the KrOH(A) minimum to that from the PES of Carter *et al.* is only for illustrative purpose, as their PES is not optimized in this region.

a) Distances in a_0, energies in cm^{-1}.
b) Present work.
c) Ref. 4.

Assignment		$E_{(4,v_s)} - E_{(4,5)}$		B_v	
(n, v_s)	$\bar{\gamma}$/degrees	Calc.	Expt.	Calc.	Expt.
(4,6)	19.7	117.1	146.1	0.11723	$\cdots$
(4,7)	21.1	220.1	277.9	0.11127	0.118893
(4,8)	23.1	308.9	393.7	0.10472	0.113949
(4,9)	27.0	383.6	491.9	0.09941	$\cdots$
(4,10)	31.8	443.5	579.7	0.08920	0.101802
(4,11)	91.7	490.3	652.9	0.08788	$\cdots$

TABLE II. Comparison of calculated (2D calculations) and experimental (Carter et al.[4]) rovibrational states and rotational constants (B_v) for Kr–HO(A). The angles, $\bar{\gamma}$, in the second column refer to vibrationally averaged values. Energies are given in cm^{-1}. Note that experimental rotational constants were not obtained for all vibrational manifolds.

Assignment		$E_{v_s} - E_5$		B_v	
v_s	γ/degrees	Calc.	Expt.	Calc.	Expt.
6	0	141.8	146.1	0.12213	$\cdots$
7	0	271.2	277.9	0.11772	0.118893
8	0	388.3	393.7	0.11306	0.113949
9	0	493.2	491.9	0.10811	$\cdots$
10	0	586.1	579.7	0.10283	0.101802

TABLE III. Comparison of calculated (1D DVR calculations) and experimental (Carter et al.[4]) rovibrational states and rotational constants (B_v) for Kr–HO(A). Energies in cm^{-1}. Note that experimental rotational constants were not obtained for all vibrational manifolds.

		RCCSD(T)			
Assignment		CC		CS	Rel. diff.
(n, v_s)	γ/degrees	Parity $+$	Parity $-$	CS	$(1, v_s) - (1, 0)$
(1,0)	180	–4347.868	–4347.375	–4347.620	0
(1,1)	180	–3906.083	–3905.597	–3905.838	441.782
(1,2)	180	–3485.411	–3484.933	–3485.170	862.45
(1,3)	180	–3085.347	–3084.876	–3085.110	1262.51
(1,4)	180	–2706.663	–2706.200	–2706.430	1641.19
(1,5)	180	–2349.772	–2349.317	–2349.543	1998.077
(1,6)	180	–2014.829	–2014.384	–2014.605	2333.015
(1,7)	180	–1702.386	–1701.951	–1702.167	2645.453
(1,8)	180	–1413.327	–1412.904	–1413.114	2934.506
(1,9)	180	–1148.871	–1148.462	–1148.665	3198.955
(1,10)	180	–910.557	–910.163	–910.359	3437.261

TABLE IV. Absolute and relative positions of HO(A)–Kr vibrational states associated with the $n = 1$ adiabatic bender curve [the lowest AB curve corresponding to states located in region of the collinear HOKr minimum ($\gamma = 180°$)], determined by CC and CS calculations for $J = 1/2$ based on our RCCSD(T) PES. Energies in cm^{-1}.

		RCCSD(T)			
Assignment		CC		CS	Rel. diff.
(n, v_s)	γ/degrees	Parity +	Parity –	CS	$(4, v_s) - (4, 0)$
(4,0)	0	−1358.135	−1357.851	−1357.992	0
(4,1)	0	−1172.364	−1172.086	−1172.225	185.767
(4,2)	0	−999.980	−999.711	−999.845	358.147
(4,3)	0	−841.164	−840.902	−841.032	516.96
(4,4)	0	−696.085	−695.832	−695.958	662.034
(4,5)	0	−564.889	−564.646	−564.767	793.225
(4,6)	0	−447.721	−447.488	−447.604	910.388
(4,7)	0	−344.664	−344.443	−344.553	1013.439
(4,8)	0	−255.810	−255.600	−255.705	1102.287
(4,9)	0	−181.149	−180.953	−181.051	1176.941
(4,10)	0	−121.085	−120.906	−120.995	1236.997
(4,11)	0	−74.559	−74.390	−74.474	1283.518

TABLE V. Absolute and relative positions of HO(A)–Kr vibrational states associated with the $n = 4$ adiabatic bender curve [the lowest AB curve corresponding to states located in region of the collinear OHKr minimum ($\gamma = 0°$)], determined by CC and CS calculations for $J = 1/2$ based on our RCCSD(T) PES. Energies in cm^{-1}.

Assignment		$E_{(4,v_s)} - E_{(4,3)}$		B_v	
(n, v_s)	$\bar{\gamma}$/degrees	Calc.	Expt.	Calc.	Expt.
(4,4)	17.8	145.1	146.1	0.12767	$\cdots$
(4,5)	18.6	276.3	277.9	0.12267	0.118893
(4,6)	19.7	393.4	393.7	0.11723	0.113949
(4,7)	21.1	496.5	491.9	0.11127	$\cdots$
(4,8)	23.1	585.3	579.7	0.10472	0.101802
(4,9)	27.0	660.0	652.0	0.09941	$\cdots$

TABLE VI. Comparison of calculated (2D CS) and experimental (Carter *et al.*[4]) rovibrational states and rotational constants (B_v) for Kr-OH(A). The energies are taken with respect to the origin of the spectrum at state (4,3) not (4,5) as in Carter *et al.*[4] Units in cm^{-1}.

Assignment		$E_{v_s} - E_3$		B_v	
v_s	γ/degrees	Calc.	Expt.	Calc.	Expt.
4	0	166.6	146.1	0.13025	$\cdots$
5	0	320.7	277.9	0.12630	0.118893
6	0	462.5	393.7	0.12213	0.113949
7	0	591.9	491.9	0.11772	$\cdots$
8	0	709.0	579.7	0.11306	0.101802

TABLE VII. Comparison of calculated (1D DVR calculations) and experimental (Carter *et al.*[4]) rovibrational states and rotational constants (B_v) for Kr–HO(A). The energies are taken with respect to the origin of the spectrum at state $v_s = 3$ not $v_s = 5$ as in Carter *et al.*[4] Energies in cm^{-1}. Note that experimental rotational constants were not obtained for all vibrational manifolds.

	F_1 levels $(j = N + \frac{1}{2})$			F_2 levels $(j = N - \frac{1}{2})$		
N	Experiment	QCT	QM	Experiment	QCT	QM
0	29(7)	38.1	—	—	—	—
1	38(7)	42.5	—	—	53.4	—
2	—	43.0	45.2	—	49.2	50.9
3	—	40.8	—	—	44.6	—
4	38(7)	39.0	41.2	39(4)	42.1	44.2
5	37(9)	36.7	36.0	38(7)	39.4	38.7
6	—	34.1	—	—	36.5	—
7	—	31.3	—	—	33.6	—
8	—	28.0	27.6	25(9)	30.2	29.9
9	—	24.7	—	—	26.8	—
14	17(9)	14.9	—	—	15.9	—

TABLE VIII. Experimentally determined thermally averaged (300 K) cross sections for RET of OH(A) by Kr. The experimental cross sections were determined by dividing the measured rate constants by the mean relative velocity at 300 K, which was taken to be $668\,\mathrm{m\,s^{-1}}$. The error bars (in parentheses) were determined using a Monte Carlo procedure[63] and represent 95% confidence limits. The experimental data are compared to the results from the QM and QCT calculations performed on the PES presented in section II. The theoretical data were obtained at a fixed collision energy of $0.039\,\mathrm{eV}$, corresponding to the mean collision energy at 300 K. The errors in the QCT data are less than 5% and typically of the order of 2-3%.

FIG. 1. (Color online) Top panel: Contour plot in the cartesian coordinates of the RCCSD(T) PES for the OH($A^2\Sigma^+$)-Kr complex calculated at the OH(A) equilibrium internuclear distance. The $2A'$ label means that this is a second excited state belonging to the A' representation of the C_s group. The energies expressed in the units of cm^{-1} are relative to the asymptotic limit of infinite separation of Kr and OH(A). Bottom panel: Contour plot in the cartesian coordinates of the A' RCCSD(T) PES for the OH($X^2\Pi$)-Kr complex calculated at the OH(X) equilibrium internuclear distance. The energies expressed in the units of cm^{-1} are relative to the asymptotic limit of infinite separation of Kr and OH(X). Note that the A'' PES is not shown, but is identical to the A' OH(X)$^2\Pi$–Kr PES at the linear configurations of the global minimum. In both panels $\gamma = 0°$ corresponds to the linear OH-Kr configuration while $\gamma = 180°$ corresponds to the HO-Kr conformer.

FIG. 2. (Color online) Comparison of the contour plots of the RCCSD(T) PESs for the OH($A^2\Sigma^+$)–Kr complex (upper panel), calculated at the OH(A) equilibrium internuclear distance, with that obtained previously in similar calculations for OH(A) + Ar (lower panel).[10]

FIG. 3. The energy level structure of free OH($A^2\Sigma^+$).

FIG. 4. (Color online) Adiabatic bender potentials for Kr-OH(A) obtained using our RCCSD(T) PES. All curves refer to a total projection quantum number $P = \frac{1}{2}$. The energies of the vibrational states in each of the three bender curves correspond, closely, to the energies obtained in full CS or CC calculations. The three curves correlate, asymptotically, with the lowest three rotational states of OH(A): $N = 0$ ($J = \frac{1}{2}$), $N = 1$ ($J = \frac{3}{2}$) and $N = 1$ ($J = \frac{1}{2}$), respectively. The $n = 2$ and $n = 3$ adiabatic bender curves are not shown in this plot, they are located in the Kr-O-H collinear minimum similarly to the $n = 0$ adiabat.

FIG. 5. (Color online) Contour plots of the wave functions of the lowest two bend-stretch states $[n = 1, v_s = 0$ (red)$]$ and $[n = 4, v_s = 0$ (black)$]$ of the Kr-OH(A) complex. The global minimum of the Kr-OH(A) corresponds to colinear KrOH geometry ($\gamma = 180°$).

FIG. 6. Experimental electronic quenching cross sections for the F_1, $j = N + 1/2$ (filled circles) and F_2, $j = N - 1/2$ (filled squares) spin-rotation levels. These are compared with previous results obtained by Hemming et $al.$ (open triangles).[14] The cross sections were measured at $300\,\mathrm{K}$ and have been determined using $\langle \sigma_{EQ} \rangle = k(T)/\langle v_\mathrm{rel} \rangle$.

FIG. 7. The fluorescence decays recorded experimentally using left and right circularly polarized light (top left), obtained using the $R_{22}(7)$ transition and a magnetic field of $20\,\mathrm{Gauss}$, or using linearly polarized light (top right), obtained using the $Q_{11}(4)$ transition without a magnetic field. Both sets of decays were recorded with $200\,\mathrm{mTorr}$ krypton. The left and right panels in the middle and bottom rows show the population decays (dashed lines), obtained from the circularly polarized probe measurements using $I_L + I_R$ (left panels), and the linearly polarized probe measurements using $I_\parallel + 2I_\perp$ (right panels). The solid lines correspond to the fits to the data, from which the RET cross sections were obtained.

FIG. 8. Left and middle panels: Opacity functions (probability $vs.$ total angular momentum) for inelastic (N-changing) scattering out of F_2 initial states ($j = N - 1/2$) at a fixed collision energy of $0.039\,\mathrm{eV}$. (Left panels) transitions which conserve the relative orientation of $\boldsymbol{N}$ and $\boldsymbol{S}$ ($\Delta j = \Delta N$), summed over all final N' states, and (middle panels) transitions which change the relative orientation of $\boldsymbol{N}$ and $\boldsymbol{S}$ ($\Delta j = \Delta N + 1$), summed over all final N' states. The right panels depict the opacity functions for the single N-conserving, spin–rotation changing transition, $j = N - 1/2 \to j' = N + 1/2$. In each panel the solid lines correspond to the open–shell CC QM data, while the QCT data are shown as dashed lines. Note that for $j = 1.5$, $J = 80$ corresponds to a classical impact parameter of $b = 4.9\,\mathrm{\mathring{A}}$.

FIG. 9. State–to–state inelastic RET cross sections out of F_2 initial spin-rotation states at a fixed collision energy of 0.039 eV for transitions which conserve the relative orientation of $\boldsymbol{N}$ and $\boldsymbol{S}$ ($\Delta j = \Delta N$) (left column) and transitions which change the relative orientation of $\boldsymbol{N}$ and $\boldsymbol{S}$ ($\Delta j = \Delta N + 1$) (right column). In each panel, the open triangles correspond to the CC QM predictions, and the open circles to the QCT predictions.

FIG. 10. RET cross sections from CC QM (open triangles) and QCT (bars) calculations out of F_1 (left panel) and F_2 (right panel) initial spin-rotation levels. The theoretical cross sections were determined at a fixed collision energy of 0.039 eV, corresponding to the mean at 300 K. The total height of the bar (and the black triangles) corresponds to the total RET cross section summed over all final N', j' states (exclusive of the purely elastic transition). The top (white) section of the bar [the difference between the triangles (black) and circles (blue)] corresponds to cross sections for transitions in which the relative orientation of $\boldsymbol{N}$ and $\boldsymbol{S}$ is changed [$\Delta N = 0$, $\Delta j = -1$ (left panel) and $\Delta N = 0$, $\Delta j = +1$ (right panel)]. The middle (blue) section of the bar [the difference between the circles (blue) and squares (red)] corresponds to the cross sections for processes in which both N and the relative orientation of $\boldsymbol{N}$ and $\boldsymbol{S}$ are changed, ($\Delta N \neq 0$ and $\Delta j = \Delta N \pm 1$). Finally the bottom (red) bar ((red) squares) are the cross sections for processes which change N, but conserve the relative orientation of $\boldsymbol{N}$ and $\boldsymbol{S}$ ($\Delta N = \Delta j$).

FIG. 11. A comparison between the (closed shell) QCT RET cross sections obtained at a fixed collision energy of 0.039 eV, corresponding to the mean at 300 K, with those obtained from the thermal rate constant (labelled 'Continuous energy'), divided by the mean relative velocity at 300 K, as given by Eq. (6).

FIG. 12. The total RET cross sections for OH(A) collisions with Kr out of the initial F_1 (left) and F_2 (right) spin-rotation levels. The experimental data (filled squares) are compared with the results from QCT (open circles) and QM (open triangles) calculations. Most of the experimental points were obtained with circularly polarized light, apart from the $N = 4$, and 5 F_1 data shown in the left panel, which employed linearly polarized light. The experimental cross sections were determined by dividing the measured rate constants by the mean relative velocity at $300\,\mathrm{K}$. The theoretical data were obtained at a fixed collision energy of $0.039\,\mathrm{eV}$, corresponding to the mean collision energy at $300\,\mathrm{K}$.

SR conserving · SR changing

$N=2, j=1.5$

$N=5, j=4.5$

$N=8, j=7.5$

QCT

QM

$\sigma_{jj'}/\text{Å}^2$

N'