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Rotationally inelastic scattering of OH($^2\Pi$) by HCl($^1\Sigma$). Comparison of experiment and theory $\dagger\dagger$

J. Klos,^a F. J. Aoiz,^a R. Cireasa^{§b} and J. J. ter Meulen^{*b}

^a Departamento de Química Física, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain

^b Department of Applied Physics, IMM, Radboud University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands. E-mail: H.terMeulen@science.ru.nl

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State-to-state integral cross sections were calculated using quantum open-shell and closed shell close coupling scattering calculations and quasi-classical trajectory calculations. Reduced dimensionality calculations for the OH–HCl system are compared to those for the OH–Ar system. We have explored the sensitivity of the cross section to the nature of the PES, using either a two-dimensional or a four-dimensional PES. Only the diagonal diabatic V_{sum} potential was used in the calculations and therefore the electronic fine structure, *i.e.* the spin–orbit and Λ -doublet structure, could not be accounted for. All the calculations were performed for the same collision energy of 920 cm⁻¹ and assuming that initially all OH molecules are in the lowest rotational state, $J = 3/2$, $\Omega = 3/2$. The theoretical results are discussed in comparison with the experimental data measured under similar conditions. The agreement of experimental results with the theoretical model based on four-dimensional close coupling calculations and treating the OH molecule as a closed-shell species is good. The validity of different proposed correspondence schemes for the transitions in OH considered as a closed-shell and as an open-shell molecule is examined by comparing the cross sections obtained for the OH + Ar system and the two-dimensional model for the OH + HCl system.

1. Introduction

Inelastic collisions of open-shell molecules have attracted considerable experimental and theoretical interest during the last decades,^{1–31} due to the importance of radicals as intermediates in a wide range of processes, such as combustion, atmospheric chemistry and astrophysics. These processes are significantly more complicated than those involving closed-shell molecules due to the presence of non-zero electronic spin and/or orbital angular momentum, which can be coupled to the nuclear rotational angular momenta of the collision partners. Furthermore, the dynamics of the systems with non-zero electronic angular momentum may entail more than one potential energy surface (PES). Therefore, while the most adequate description would imply quantum mechanical methods, a quasi-classical description would have to consider that the collision ‘trajectories’ evolve simultaneously and coherently on the coupled PESs.³² Particularly, it was found that in the collision processes between a $^2\Pi$ diatomic molecule and a noble gas, the cylindrical degeneracy of the former is lifted by the approach of the colliding atom giving rise to two PESs of A' and A'' symmetry.^{21,23,25} The collision induced fine-structure and rotational distributions depend sensitively on these PESs. The resulting spin–orbit and lambda doublet propensities are often reflections of the interferences between collisions sampling, to

different extents, one or the other potential energy surface.^{8,23,24} Alexander has shown that for molecules in Hund’s case (a) the spin–orbit conserving transitions are governed by the sum of these potentials, while the spin–orbit changing transitions are governed by their difference.^{23,24} The difference potential is smaller in magnitude and so are the spin–orbit changing cross sections. This formalism developed for scattering by rare gas atoms is not always valid when the scattering partner is a molecule. The system contains non-planar geometries which leads to a complicated PES depending strongly on the relative orientation of the colliding molecules. To date, there are several theoretical studies approaching the inelastic scattering of radicals by different atomic or molecular colliders^{8,20,21} at a quantum mechanical level. By far the largest body of theoretical work, also backed up by different types of experiments, concerns the scattering of NO by Ar and He.^{19,25,31,33–36} Similar calculations have been performed for the OH + Ar/He systems.^{15,16,30} However, due to their greater complexity, studies of molecule–molecule collisions are scarce. Most of these studies concern the rotational excitations of the OH + H₂ system, which present a great astrophysical interest.^{28,29,37}

Reactions of OH with hydrogen halides are the major sink for halogens from the atmosphere, and are known as efficient re-converters to the active forms of the halogens. These active halogens can further participate in the catalytic ozone destruction in the stratosphere. In particular, the OH + HCl reaction is the primary process that releases active chlorine in the atmosphere. Therefore, the reaction rate of this process controls the steady state Cl concentration in the stratosphere. Consequently, the important role played by the OH + HCl reaction in atmospheric chemistry has given rise to a wealth of experimental and theoretical studies concerning the reactivity of this system. Quantitative information on the reactivity of the

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\ddagger Electronic supplementary information (ESI) available: Fig. 2 in colour. See <http://www.rsc.org/suppdata/cp/b4/b411309h/>

\S Present address: Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QZ. Permanent address: National Institute for Laser, Plasma and Radiation Physics, Laser Department, P.O. Box MG-36, Bucharest, Romania.

OH + HCl system is provided by an extensive set of kinetic experiments in which temperature dependent rate constants were measured over a wide temperature range.^{38–45} Several theoretical studies have been published in which the OH + HCl system is treated at different levels of theory in order to develop the PES governing the interaction and to calculate the rate constants and the reaction cross sections.^{46–50} Clary *et al.*⁴⁶ carried out quantum scattering calculations using the rotating bond approximation (RBA) on a semi-empirical potential surface with a classical energy barrier of 0.25 kcal mol⁻¹. Steckler *et al.*⁴⁷ have performed variational transition-state theory calculations using scaled *ab initio* data to define the minimum energy path (MEP). Using a coupled cluster with single, double and non-iterative triple excitations (CCSD(T)/PVQZ) method, they obtained a reaction barrier of 2.43 kcal mol⁻¹. Yu and Nyman⁴⁸ carried out dynamical calculations using the RBA approach on a new PES obtained by interpolation of *ab initio* energy values computed using an unrestricted Møller–Plesset (UMP2) method and scaling correction. Their PES exhibits an early barrier of 2.06 kcal mol⁻¹ and a planar Van der Waals complex with a well of -5.46 kcal mol⁻¹. The most recent theoretical calculations^{49,50} use the ‘largest angle generalization of the rotating bond order’ (LAGROBO) functional formulation of the interaction between OH and HCl in order to shape the PES. The parameters of the PES were adjusted in order to minimize the difference between the values of the rate constants obtained using quasi-classical trajectory (QCT) calculations and experimental values.

Motivated by the importance of the OH–HCl system, we have performed an experimental and theoretical study of the non-reactive dynamics of the OH + HCl system. Experiments carried out in a crossed molecular beam setup⁵¹ provide relative cross sections for collision induced transitions from the ²Π_{3/2}, *J* = 3/2, f state of OH up to ²Π_{3/2}, *J* = 9/2 and ²Π_{1/2}, *J* = 5/2. Theoretical state-to-state integral cross sections were calculated by employing both quantum mechanical and quasi-classical approaches of the scattering process, on a new developed non-reactive PES. In addition, the quantum mechanical closed coupled scattering formalism used both open-shell and closed-shell approximations. We have explored the sensitivity of the cross section to the nature of the PES, by employing either an effective two-dimensional or a four-dimensional PES. The electronic fine structure, *i.e.* the spin–orbit and *A*-doublet structure, was not explicitly treated as only the spin and orbital angular momentum averaged potential was used in the scattering calculations. All the calculations were performed for the same collision energy of 920 cm⁻¹ and assuming that all molecules are in the lowest rotational state, *J* = 3/2, as in the recent experiments.⁵¹

2. Quantum and quasi-classical calculations

2.1. *Ab initio* calculation and modeling of the PES of OH–HCl

Only a brief description of the *ab initio* procedure used to obtain the OH–HCl potential energy surface (PES) will be presented here; a detailed account will be given elsewhere.⁵² For the electronic structure calculations, we use the partially spin-restricted coupled cluster method with single, double and perturbational triple excitations (RCCSD[T]) implemented in the MOLPRO⁵³ suite of programs. The basis set was chosen to be an augmented, correlation consistent, double-zeta basis with additional bond functions 3s3p2d centered in the middle of the vector *R* that connects the OH and the HCl centers of mass. The open-shell nature of the OH radical gives rise to two adiabatic solutions of the electronic Hamiltonian from which the diabatic diagonal surface was obtained. The interaction energy was calculated using the supermolecular approach including the application of the counterpoise correction

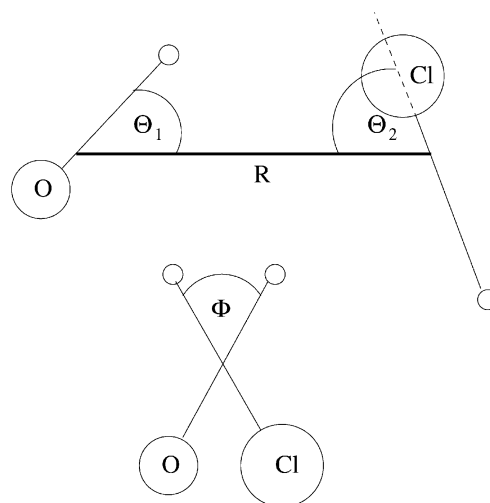


Fig. 1 Jacobi coordinates for the OH–HCl system.

procedure of Boys and Bernardi⁵⁴ to remove the basis set superposition error.

The geometry of the system is described in Jacobi coordinates as shown in Fig. 1. The θ_1 and θ_2 angles correspond to the angles between the OH and HCl axes, respectively, and the intermolecular vector *R*, and the angle ϕ is the dihedral angle between the *R*–*R*_{OH} and *R*–*R*_{HCl} planes. The geometry ($\theta_1 = 0$, $\theta_2 = 0$, $\phi = 0$) corresponds to the OH...ClH linear configuration. The intermolecular distance *R* is the length of *R*. Formally, the PES for the OH–HCl system is six dimensional. In the 4D PES both OH and HCl are treated as rigid rotors with the internuclear distances frozen to their equilibrium values, 1.032 and 1.275 Å, respectively.

The *ab initio* points were fitted and expanded as a series of spherical harmonics, based on a modification of the expansion given in ref. 52

The diagonal diabatic potential *V*_{sum} was obtained by arithmetic averaging of two adiabatic solutions of the electronic Hamiltonian for each geometry considered in the calculations. The averaging produces a single PES which effectively treats OH as a closed shell molecule.

The well depth of the Van der Waals minimum found on this PES is ≈ 860 cm⁻¹. The geometry associated to the minimum corresponds to a hydrogen bonding of the hydrogen atom of HCl to the oxygen site of the OH radical. The geometry is planar ($\phi = 180^\circ$) with Jacobi orientation angles for the OH and HCl of $\theta_1 = 130^\circ$ and $\theta_2 = 170^\circ$, respectively. The equilibrium distance for this geometry is $R_e \approx 6.4 a_0$. The more detailed calculations from ref. 52 indicate that the global van der Waals minimum is somewhat shifted in comparison to the PES used in this study. More recently, an inaccuracy in the PES has been found, corresponding to an artificial barrier between the geometry of the global minimum reported here and the linear minimum. The new results from the ref. 52 seem to indicate that such a barrier with a height of 140 cm⁻¹ does not exist. It remains to be established whether the cross sections will be affected by such details of the PES. Future studies on the improved potential surface could answer this question.

Additionally, we have generated a 2D-PES by averaging the 4D OH–HCl PES over (θ_2 , ϕ) coordinates, in order to make a comparison at the same collision energy between the scattering of the OH by HCl and by ³⁶Ar. The contour plot of this 2D PES, *V*_{OH–X}(*R*, θ_1), where X represents the HCl molecule considered as a spherically symmetric target, is shown in Fig. 2. This 2D PES is very similar to the OH–Ar *V*_{sum} diabatic potential presented in,⁵⁵ with a global minimum for the linear OH–X geometry as in the case of OH–Ar, and with a well depth of similar order.

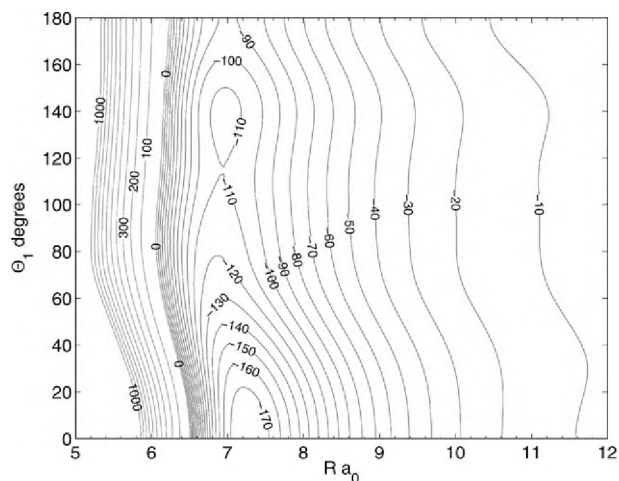


Fig. 2 Contour plot of the 2D OH–HCl PES after averaging over the θ_2 and ϕ coordinates. The global minimum of this PES is $D_e = 179 \text{ cm}^{-1}$ for $R_e = 7.3 a_0$ for collinear geometry with $\theta_1 = 0^\circ$. There is a local minimum with a well depth of 133 cm^{-1} for $R = 6.95 a_0$ and $\theta_1 = 138^\circ$. Contours in cm^{-1} .

The comparison between the inelastic cross sections obtained using the 2D PES for the OH–HCl interaction and those calculated for the OH–Ar system may shed some light on the differences and analogies between these two systems. Open-shell calculations for the OH–Ar system have been performed by both including the $V_{\text{diff}} = 1/2 (A'' - A')$ surface and neglecting it. To compare the OH–X system (X stands for the spherically symmetric HCl molecule) with the OH–Ar system we used the UMP4 diabatic V_{sum} PES of Klos *et al.*⁵⁵

2.2. Methodology of scattering calculations

To calculate integral cross sections for the inelastic collisions between OH and HCl we used both full quantum close coupling calculations and quasi-classical trajectory calculations.

In order to perform these calculations we used the V_{sum} part of the potential corresponding to the diagonal elements of the potential diabatic matrix of either the 4D or the 2D PES.

The 2D OH–HCl PES, obtained as described above, was used to assess the model approximations employed for the calculations. In this model, the HCl molecule is treated as a spherically symmetric target, and thus becomes similar with the isoelectronic OH–³⁶Ar system. For a more accurate comparison the Ar isotope of mass 36 has been chosen. Of course, the HCl molecule has significant electrostatic multipole moments and thereby differs from the Ar atom. In the 2D full quantum close coupling (CC) approach we treat the OH molecule as an open-shell species, using the basis included in the Hibridon package⁵⁶ and as a closed shell species using the scattering MOLSCAT program.⁵⁷ For the case of the open-shell calculations we neglect the off-diagonal diabatic coupling surface V_{diff} . All the partial waves up to the total angular momentum quantum number $J_{\text{tot}} = 350.5$ ($J_{\text{tot}} = 350$ for the closed shell case) were included in the close-coupling calculations performed at $E_{\text{col}} = 920 \text{ cm}^{-1}$. Only the rotational levels of the OH molecule up to $J' = 8.5$ (8 for closed shell) were considered. The close coupling calculations were performed using the hybrid propagator composed of log-derivative and Airy propagators.

The quasi-classical dynamics calculations were performed on the 2D PES by using the QCT-ABC program developed by Aoiz *et al.*^{58,59} A convergence in the integral cross sections of the order of 10^{-2} \AA^2 could be obtained with 1.12×10^5 trajectories.

The comparison between the cross sections obtained with the open-shell approach and those obtained with the closed-shell

approach is not always unequivocal. One has to define the correspondence between $j = 0 \rightarrow j'$ transitions, where j is the nuclear rotational angular momentum, used for the closed-shell model, and $J \rightarrow J'$ transitions of an open-shell system, where J is the total angular momentum for OH including the orbital and spin components. In Hund's case (a), the rotational state of an open-shell molecule is characterized by J and Ω , the latter being the sum of the projections of the electronic orbital and spin angular momenta. In addition, each $|J, \Omega\rangle$ state is split in two A -doublet components. On the other hand, the OH total angular momentum excluding the spin is given by $N = j + \Lambda$, where Λ ($|\Lambda| = 1$ for the OH ground electronic state) is the projection of the electronic angular momentum along the internuclear axis of the OH molecule.

The most straightforward correspondence consists in equating Δj to ΔJ . This procedure has been applied before for systems whose ground state is $|J, \Omega, \epsilon\rangle = |1/2, 1/2, \epsilon\rangle$, as in the case of the NO molecule.⁵⁹ In the case of the OH molecule, the spin-orbit doublet is inverted and the ground-state is therefore $|3/2, 3/2, e\rangle$. The equivalent correspondence is thus $\Delta j = \Delta J + 1$. However, several problems arise when using this correspondence. Firstly, a given N , and thus a j value, correlates with two different J states, depending on the value of Ω , neglecting for the moment the A -doublet splitting. Secondly, the energies for a given J value differ considerably depending on the Ω value, even for high J values. Finally, the transition from the $|3/2, 3/2, f\rangle$ state to the $|3/2, 3/2, e\rangle$ state can not be considered as an elastic collision in spite of being characterized by the same values of J and Ω .

An alternative correspondence is based on the relation between N (or j) and J and Ω values and is represented in Table 1. The first two rows of the table correspond to $j = 0$, which is the initial state in the case of the closed-shell calculations. In order to compare the closed-shell cross sections to open shell ones, according to Table 1, one would have to consider several open-shell transitions for each closed-shell transition. Particularly, for the $j = 0 \rightarrow j' = 1$ transition the cross section correspondence will be defined as follows (summing over the A -doublet components of the final states and averaging over the A -doublet components of the initial state):

$$\begin{aligned} \sigma(0 \rightarrow 1) = & 1/2 \sum_{\epsilon, \epsilon'} [\sigma(3/2, 3/2, \epsilon \rightarrow 3/2, 1/2, \epsilon') \\ & + \sigma(3/2, 3/2, \epsilon \rightarrow 5/2, 3/2, \epsilon') \\ & + \sigma(1/2, 1/2, \epsilon \rightarrow 3/2, 1/2, \epsilon') \\ & + \sigma(1/2, 1/2, \epsilon \rightarrow 5/2, 3/2, \epsilon')] \end{aligned} \quad (1)$$

Table 1 Quantum numbers used to describe the rotational states of OH molecule

J	Ω	N	j
1/2	1/2	1	0
3/2	3/2	1	0
3/2	1/2	2	1
5/2	3/2	2	1
5/2	1/2	3	2
7/2	3/2	3	2
7/2	1/2	4	3
9/2	3/2	4	3
9/2	1/2	5	4
11/2	3/2	5	4
11/2	1/2	6	5
13/2	3/2	6	5
13/2	1/2	7	6

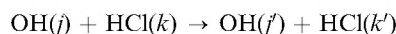
Similarly, for the $0 \rightarrow 2$ transition the following open-shell transitions would have to be considered:

$$\begin{aligned} \sigma(0 \rightarrow 2) = & 1/2 \sum_{\varepsilon, \varepsilon'} [\sigma(3/2, 3/2, \varepsilon \rightarrow 5/2, 1/2, \varepsilon') \\ & + \sigma(3/2, 3/2, \varepsilon \rightarrow 7/2, 3/2, \varepsilon') \\ & + \sigma(1/2, 1/2, \varepsilon \rightarrow 5/2, 1/2, \varepsilon') \\ & + \sigma(1/2, 1/2, \varepsilon \rightarrow 7/2, 3/2, \varepsilon')] \end{aligned} \quad (2)$$

The various $|J, \Omega\rangle$ states correlating with the same N have much closer energies than those corresponding to the same value of J . Moreover, this difference becomes smaller as N increases, and the OH angular momentum coupling is no longer well described by Hund's case (a). The two correspondence schemes will be thoroughly discussed in Section 4.

2.3. 4D closed shell calculations

To include the effect of the rotational channels of the HCl molecules the 4D OH–HCl PES was used. This potential was interfaced to the MOLSCAT⁵⁷ program with a diatom-diatom closed shell basis type. Originally, to calculate the potential for every point it was necessary to solve a large system of algebraic equations. That resulted in an excessively long CPU time. In order to speed up the calculations with the 4D potential, we extracted the radial coefficients, fitted them to radial functions of the Degli-Esposti and Werner type⁶⁰ and used them in a direct expansion in spherical harmonics. A typical error of the fit of the coefficients ranges from 10^{-3} cm^{-1} to 164 cm^{-1} for the long-range and medium range dependence on R and the very short range, respectively. This procedure allowed to calculate the integral cross sections in a reasonable time. To calculate integral cross sections, $\sigma_{j'j}$, for the collision induced excitations of the OH radical ($j \rightarrow j'$) the cross sections for all energetically allowed transitions



were calculated. Subsequently, to determine $\sigma_{j'j}$ one needs to sum over all final HCl k' states and average over the initial distribution of the HCl (k) rotational states.

The averaging was done by using a rotational partition function for the temperature corresponding to the experimental conditions ($T = 20.5 \text{ K}$):

$$\sigma_{j'j} = \frac{1}{\Xi} \sum_{kk'} \sigma_{jk \rightarrow j'k'} (2k+1) e^{-Bk(k+1)/k_B T} \quad (3)$$

where Ξ is the rotational partition function:

$$\Xi(T) = \sum_k (2k+1) e^{-Bk(k+1)/k_B T} \quad (4)$$

and B is the rotational constant of the HCl molecule ($B = 10.593 \text{ cm}^{-1}$).

In the scattering calculations at $E_{\text{col}} = 920 \text{ cm}^{-1}$ we summed all the partial waves up to the total angular momentum $J_{\text{tot}} = 350$ in steps of $\Delta J_{\text{tot}} = 10$ to reduce the calculation time. The rotational basis consists of 205 open channels and includes functions with j up to 6 and with k up to 8.

3. Experiment

The experiments were carried out in a pulsed crossed molecular beam machine at a collision energy of 920 cm^{-1} . The experimental setup is described in detail elsewhere⁵¹ and is similar to the one used before in studies of collisions of OH with Ar¹⁵ and other species.¹³ The OH radicals are produced in an electrical discharge in the expansion of a H₂O/Ar mixture. Prior to the collisions, the OH radicals were prepared in a single quantum

Table 2 Experimental state-to-state integral cross sections for OH–HCl system⁵¹ in arbitrary units

J'	Ω'	ε'	σ
3/2	3/2	e	55.36 ± 1.43
5/2		e	6.28 ± 0.21
5/2		f	6.48 ± 0.28
7/2		e	1.76 ± 0.15
7/2		f	1.75 ± 0.16
9/2		e	0.49 ± 0.10
9/2		f	0.82 ± 0.30
1/2	1/2	e	1.49 ± 0.08
1/2		f	1.47 ± 0.20
3/2 + 5/2		e ^a	1.78 ± 0.12
3/2		f	0.82 ± 0.08
5/2		f	1.30 ± 0.24
7/2		e	0.87 ± 0.10

^a Not resolved experimentally.

state by combining the supersonic cooling with the electrostatic state selection in a hexapole. The electrical field created in the hexapole focus in the collision region only those OH molecules in the $\Omega = 3/2$, $J = 3/2$, f state, while deflecting the molecules in the lower A -doublet e states from the beam axis. As the molecules in the upper A -doublet f states of the excited rotational states were only weakly focused, about 94% of the OH radicals entering the collision zone are in the $|3/2, 3/2, f\rangle$ state. The pulsed HCl beam intersects the OH beam at right angle. A rotational temperature of the HCl beam of 20.5 K was inferred from $(1 + 1')$ REMPI spectra. Both the initial and final state distribution of the OH radicals were probed by saturated laser induced fluorescence (LIF) detection of the 0–0 band of the $A^2\Sigma^+ - X^2\Pi$ transition at 308 nm. Relative state-to-state cross sections were measured at a mean collision energy of 920 cm^{-1} for rotational excitations up to $J = 9/2$ in the $\Omega = 3/2$ spin-orbit manifold and up to $J = 7/2$ in the $\Omega = 1/2$ spin-orbit ladder. These relative cross sections (in arbitrary units), given in Table 2, show the usually observed energy gap law dependence on the final rotational state. As generally found in inelastic scattering of OH the cross sections for spin-orbit conserving transitions are stronger than for spin-orbit changing transitions. Whereas for other collision partners such as for He¹¹ and Ar¹⁵ a clear propensity for e-states is observed, in the case of the OH–HCl system no preference for excitation into one or the other A -doublet components of a final rotational state was measured. This may be ascribed to the longer range of the mutual interaction, determined mainly by the dipole-dipole interaction, as compared to the other systems studied thus far. These results are extensively discussed in a separate paper.⁵¹

4. Results and discussion

The comparison between experimental and 4D closed-shell integral cross sections is shown in Table 3 and displayed in Fig. 3. In order to perform this comparison, experimental cross

Table 3 Comparison of the OH–HCl four-dimensional closed-shell (in \AA^2) and scaled experimental integral cross sections

Δj	J'	Closed-shell CC 4D ^a	Experiment (scaled ^b)
1	3/2	73.56	64.71 ± 1.67
2	5/2	9.01	14.92 ± 0.41
3	7/2	2.27	4.10 ± 0.26
4	9/2	0.42	1.53 ± 0.37

^a Closed shell close coupling (CC) calculations on V_{sum} 4D PES.

^b Scaling with a factor resulting by equating the sums of theoretical and experimental $\Delta\Omega = 0$ cross sections.

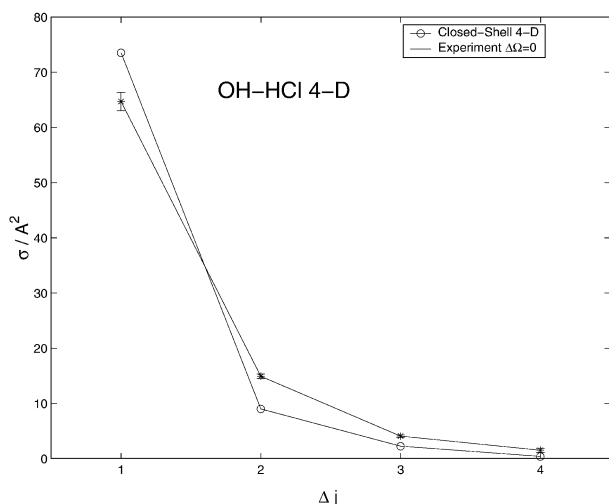


Fig. 3 Comparison between theoretical 4D close coupling calculations considering OH as a closed shell molecule (open circles) and experimental relative state-to-state integral cross sections (stars) at $E_{\text{coll}} = 920 \text{ cm}^{-1}$ collision energy. The correspondence between closed and open shell transitions is described in the text. The experimental cross sections have been scaled to the theoretical values as indicated in the text.

sections for spin conserving transitions ($\Delta\Omega = 0$) were summed over the two A components. For the first inelastic transition it was assumed that the closed shell $0 \rightarrow 1$ transition can be ascribed to the $|3/2, 3/2, f\rangle \rightarrow |3/2, 3/2, e\rangle$ transition. For the rest of the transitions it was implicitly assumed that $\Delta j = \Delta J + 1$. The factor used to scale the experimental cross sections to the theoretical ones was chosen to be the ratio between the sum of the theoretical cross sections and the sum of the experimental cross sections.

The agreement obtained is acceptable. The largest relative deviation corresponds to $\Delta j = 1$, for which theory predicts a cross section well above the experimental value, even if the uncertainty of the measurement is taken into account. For $\Delta j > 1$, the theoretical cross sections are below the experimental ones.

The calculated trend is similar for the two sets of data, with the cross section decreasing rapidly for the first two transitions and then leveling off for transitions to higher J states.

In spite of the relative agreement, the assumed correspondence between transitions for closed and open shell molecule based on $\Delta j = \Delta J + 1$, when the ground rotational state is $J = 3/2$, is somewhat arbitrary and far from being satisfactory. The difference between the energy levels of the f and e A -doublet components is merely -0.67 cm^{-1} , whereas the closed-shell transition $0 \rightarrow 1$ implies a positive energy difference of 37.82 cm^{-1} .

The alternative correspondence scheme proposed in Section 2.2, based on the value of the N quantum number, cannot be used for the comparison between the present 4D calculations and the experimental results as it requires the knowledge of the cross sections for the scattering out of the $|1/2, 1/2, e\rangle$ state which are not experimentally available.

To check the reliability of the comparison carried out above, calculations have been performed at the same collision energy of 920 cm^{-1} , for the OH-Ar system. Both open-shell to closed-shell correspondence schemes described in Section 2.2 have been applied. Table 4 contains the cross sections for the OH-Ar system calculated by employing different models by using both open and closed shell CC calculation methods. The second column displays the values of the cross sections presented using the same correspondence scheme as in Table 3 and only the spin-orbit conserving transitions. The sixth column displays the values obtained on the V_{sum} PES, considering OH

Table 4 Comparison of the OH- ^{36}Ar system closed-shell and open-shell integral cross sections calculated at $E_{\text{coll}} = 920 \text{ cm}^{-1}$

J'	Open-shell $\Delta\Omega = 0^a$	Δj	Open-shell CC 1 ^b	Open-shell CC 2 ^c	Closed-shell CC ^d
3/2	9.40	1	25.27	13.75	12.47
5/2	12.48	2	10.47	7.66	6.08
7/2	2.96	3	3.87	4.85	4.29
9/2	0.84	4	1.26	1.44	2.15
11/2	0.39	5	0.10	0.05	1.01

^a Only transitions from $|3/2, 3/2, f\rangle$ states taken into account and summed over final A -doublet states for $\Omega' = 3/2$ manifold. ^b Open-shell close coupling calculations. Integral cross sections averaged over initial and summed over final parities. V_{diff} PES is included in the calculations. ^c Open shell calculations. Integral cross sections averaged over initial and summed over final parities. V_{diff} PES was neglected. ^d Closed shell close coupling (CC) calculations on V_{sum} PES.

as a closed-shell molecule and labeling the transitions according to their Δj value. As can be seen, the agreement is very poor. Interestingly, the nearly elastic $|3/2, 3/2, f\rangle \rightarrow |3/2, 3/2, e\rangle$ transition has a cross section lower than that corresponding to the $|3/2, 3/2, e\rangle \rightarrow |5/2, 3/2, f/e\rangle$ transition, in strong contrast with the experimental results for the OH-HCl system. This can be attributed to the fact that the collision with HCl implies strong dipole-dipole anisotropic interactions which may favor the first transition.

The remaining columns of the table show the cross sections calculated by treating OH as an open-shell molecule and using the correspondence of eqns. (2) and (3). In this case, the spin-orbit changing transitions were also included.

The comparison with the closed-shell CC cross section is displayed in Fig. 4. The best agreement is obtained for the calculations using only the V_{sum} potential. This is not surprising since the closed-shell calculations involve only that part of the PES. On the other hand, the comparison with the results obtained by considering the full PES, suggests that the effect of

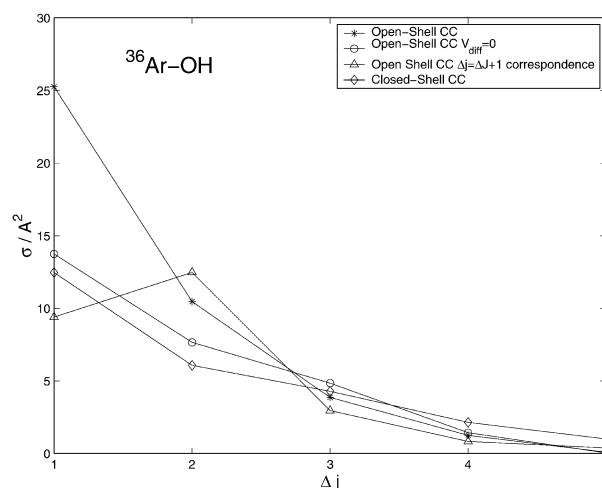


Fig. 4 Comparison between theoretical state-to-state integral cross sections for the OH- ^{36}Ar system calculated at $E_{\text{coll}} = 920 \text{ cm}^{-1}$ collision energy using different models and the Δj corresponding rules. The cross sections are averaged over initial and summed over final A -doublet states and obtained from correspondence rules according to Δj as indicated in the text. The results are shown for open shell close coupling calculations (stars), open-shell close coupling calculations neglecting V_{diff} surface (open circles) and closed shell close coupling calculations (diamonds). The triangles represent cross sections obtained by using open shell close coupling calculations with full PES averaging over initial and summing over final A -doublet states for $\Delta\Omega = 0$ transitions using $\Delta j = \Delta J + 1$ correspondence scheme.

Table 5 Comparison of the OH–HCl two-dimensional closed-shell and open-shell integral cross sections calculated at $E_{\text{coll}} = 920 \text{ cm}^{-1}$

J'	Open-shell CC 2D ^a	Δj	Open-shell CC 2D ^b	Closed-shell CC 2D ^c	QCT 2D ^d
3/2	17.2	1	18.31	18.18	23.57
5/2	8.07	2	10.24	10.04	10.37
7/2	3.99	3	5.83	5.71	4.25
9/2	2.11	4	1.99	2.58	3.49
11/2	0.71	5	0.10	1.0	2.84

^a Open shell calculations. Integral cross sections averaged over initial and summed over final parities and using the correspondence scheme $\Delta j = \Delta J + 1$. V_{diff} PES was neglected. ^b Open shell calculations. Integral cross sections averaged over initial and summed over final parities using ΔN correspondence scheme. V_{diff} PES was neglected. ^c Closed shell close coupling (CC) calculations on V_{sum} PES. ^d Calculations on V_{sum} two-dimensional PES.

the V_{diff} (4th column) is to increase the cross section values for the lowest transitions.

Calculations have also been carried out for the 2D model of the OH–HCl system, considering HCl as a spherically symmetric target, and only taking into account the V_{sum} potential. The results shown in Table 5 and in Fig. 5, obtained with the correspondence based on N values instead of J are in very good agreement with those corresponding to transitions calculated assuming OH as a closed-shell molecule. As it can be seen, the results obtained with the correspondence scheme based on the $\Delta j = \Delta J + 1$ (second column in Table 5) assignment are in substantially worse agreement with the closed-shell calculations. Finally, the comparison of QCT and closed-shell QM cross sections indicates that the QCT data account for the general trend but clearly overestimate the values corresponding to the $\Delta j = 1$ transition.

It is interesting to see how the reduced dimensionality of the PES affects the magnitude of the cross sections. Therefore, we consider further a comparison between the results of the 2D and 4D closed-shell calculations. As expected, the $\Delta j = 1$ cross section is strongly underestimated by the 2D calculations. However, the contrary applies for transitions with higher Δj .

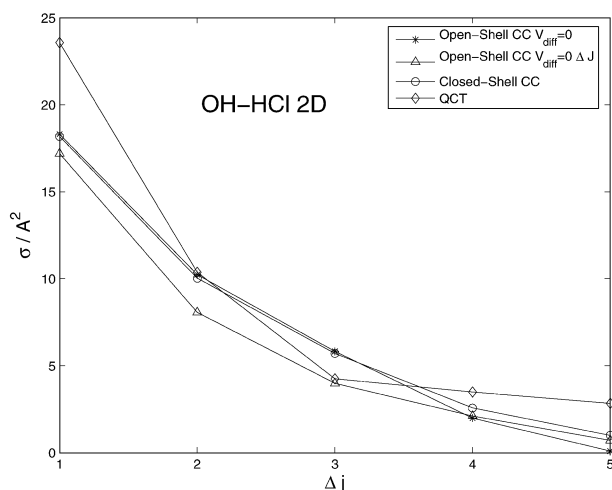


Fig. 5 Comparison between theoretical state-to-state integral cross sections for the OH–HCl system calculated using 2D PES at collision energy $E_{\text{coll}} = 920 \text{ cm}^{-1}$. The cross sections are averaged over initial and summed over final A -doublet states and obtained from correspondence rules according to Δj as indicated in the text. The results are shown for open shell close coupling calculations neglecting V_{diff} surface (stars), open shell cross sections assigned according to $\Delta j = \Delta J + 1$ values (triangles), closed shell close coupling calculations (open circles) and quasi-classical (QCT) calculations (diamonds).

Clearly, for these transitions, the presence of rotational degrees of freedom of the HCl that can be excited by collisions may prevent a more efficient flow of the translational into rotational energy as it happens for a structureless collision partner. In addition, the deeper long-range attractive potential well in the 4D potential is expected to favour low Δj transitions as compared to the shallower 2D potential resulting from the averaging of the 4D PES.

As for the comparison between the isoelectronic OH–³⁶Ar and 2D OH–HCl systems, the cross sections are smaller for the former, especially for the lowest transitions. The OH–Ar PES is approximately 30 cm^{-1} shallower than the 2D PES averaged over the HCl rotations and this might be responsible for this difference.

On the basis of the present results, it can be concluded that the comparison between the experimental and theoretical results obtained by considering OH as closed-shell molecule depends strongly on the correspondence between open and closed-shell transitions. The integral cross sections presented here seem to indicate that the assignment based on the N values is somewhat more consistent than that using the J values, but even this procedure is not exempt from some arbitrariness. An accurate assessment of the present PES demands full CC calculations considering all the angular momenta involved. For reactive systems the situation might not be so serious since more complex processes are involved and one would expect some average on the final conditions; additionally reactive processes usually involve the population of many states and transitions with large N' .

The above results do not rule out completely the possible concurrence of reactive scattering. However, considering the order of magnitude of the cross sections for inelastic processes into low J , it is unlikely that reactive scattering would play a major role in depleting final OH states. Reactive scattering involves collisions at smaller impact parameters than the excitation into low J states. Both complex formation/decomposition and reactions will affect more the cross sections to higher J states.

5. Summary

In this study we present a first attempt to compare recent experimental results of state-to-state inelastic scattering measurements⁵¹ with theoretical calculations based on a recent high-level *ab initio* potential energy surface. Close coupling QM four-dimensional calculations treating the OH radical as a closed-shell molecule have been performed on this PES. This approximation gave a fairly good agreement with the experimental values. The general trend of the cross-sections is well reproduced. Nevertheless, the correspondence between the closed-shell and open-shell transitions is not straightforward. To assess the validity of the various possible correspondence schemes we carried out reduced dimensionality calculations for the OH–HCl and the isoelectronic OH–³⁶Ar systems at the same collision energy. The results obtained seem to indicate that the correspondence based on $N = j + A$, where j is the nuclear rotational angular momentum of the diatomic molecule, accounts better for the comparison between the open-shell and closed-shell approaches.

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