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State-to-state cross sections for rotational excitation of OH by collisions with He and Ar

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Parity resolved state-to-state cross sections for rotational excitation of OH($X^2\Pi$) colliding with He and Ar, have been obtained in a crossed molecular beam experiment. The OH radicals were produced in a pulsed dc discharge in a H₂O/Ar gas mixture. Adiabatic expansion into vacuum resulted in an effective rotational cooling yielding a 94% population of the lowest Λ -doublet ($X^2\Pi_{3/2}$, $J=\frac{3}{2}$). Further state preparation could be achieved via electrostatic state selection in a hexapole electric field, resulting in a 93.5% population of the upper Λ -doublet component ($f, +$). Experiments were performed both with and without the state selector to provide detailed information about the rotational excitation from both Λ -doublet states. The OH rotational state distribution was probed, before and after the collision event, by means of laser-induced fluorescence (LIF) spectroscopy of the $A \leftarrow X$ electronic band at 308 nm. The OH-Ar and OH-He scattering behave very similar with the exception of the $J=\frac{3}{2}$ Λ -doublet transition which is induced much weaker by the He collisions. For both collision systems the experimental results are in agreement with theoretical cross sections obtained from quantum scattering calculations of Werner *et al.* [J. Chem. Phys. (submitted)].

I. INTRODUCTION

Inelastic scattering of open shell diatomics has become a subject of considerable interest in current experimental and theoretical work on molecular dynamics. At the experimental side the fast development of efficient state selective laser detection techniques in combination with pulsed supersonic molecular beams has made possible the measurement of state-to-state cross sections for rotational energy transfer. Furthermore, efficient pulsed sources of free radical beams have become available making this field now also accessible for the study of scattering of chemically unstable species. A strong impetus to the progress of theory in this field has been given by the recent observations of weakly bound open shell van der Waals complexes which are nowadays one of the main topics in molecular spectroscopy. The spectroscopy of these van der Waals molecules as well as the dynamics of the collision process are governed by the same physical quantity, i.e., the potential describing the intermolecular interactions.

Of all the open shell species the OH molecule probably is the most frequently studied and consequently best understood free radical. As an intermediate species in many chemical reactions it plays a crucial role in various processes which are of fundamental importance like in combustion, plasmas, chemical vapor deposition, and in the atmosphere. The study of the collision dynamics of OH is essential to understand and eventually control these processes. In the interstellar space the rotational energy transfer of OH by collisions with H₂ is one of the basic processes which are thought to be responsible for the observed anomalous Λ -doublet emissions from this molecule.

Despite of its relevance the rotational energy transfer of OH in the electronic ground state $X^2\Pi$ has practically not been studied so far. Recently Andresen *et al.*¹ pub-

lished the results from a crossed beam collision experiment in which they prepared the lowest rotational state $J=\frac{3}{2}$ of OH($X^2\Pi_{3/2}$) as the initial state in the primary beam. Parity averaged cross sections were obtained for rotational excitation of OH by collisions with H₂ and D₂. The most interesting result was the observation that one of the Λ -doublet states of the final rotational state is preferred. Similar propensities were observed by MacDonald and Liu² in state-to-state inelastic scattering of CH($X^2\Pi$) by He. The electronic structure of the CH radical resembles the one of OH but with only one instead of three π electrons in the outer shell, and as such similar scattering results might indeed be expected. The initial state preparation in their and Andresen's experiment is based on rotational cooling in a supersonic expansion. This results in the occupation of mainly the lowest rotational state. Since this state is split into two nearly equally populated Λ -doublet states the results obtained are parity averaged cross sections with respect to the initial state. The e/f preferences observed must therefore be due to different propensities for transitions out of the two Λ -doublet states. It was shown by Alexander³ that the collision process of a $^2\Pi$ diatomic molecule and an atom can be described by two potential surfaces, $V_{A'}$ and $V_{A''}$, which are symmetric and antisymmetric, respectively, with respect to a reflection in the plane containing the diatom and the collision partner. The observed e/f preferences can be ascribed to quantum interference effects between the scattering amplitudes for these two potential surfaces.⁴

In the present study the OH molecule is prepared in a single Λ -doublet state which makes a more direct test of calculated potential surfaces $V_{A'}$ and $V_{A''}$ possible. In addition the size of the collision induced Λ -doublet transition can be determined relative to rotational excitation. This was not possible in the experiment of Andresen *et al.* and

MacDonald and Liu since both Λ -doublet states of the initial rotational state were equally populated. Up to our knowledge the only other parity resolved collision work on OH is the double resonance relaxation experiment of Crosley and co-workers.⁵ They obtained rate coefficients for rotational energy transfer of OH ($X^2\Pi$) in the $v=2$ vibrational state by He. A propensity for parity conservation was found for spin-orbit multiplet changing collisions. Andersen *et al.* have tried to measure the relative strength of Λ -doublet transitions by preparing the upper $J=\frac{3}{2}$ Λ -doublet state in $v=1$ in a double resonance experiment.¹ Due to a weak sensitivity only indications were obtained that the Λ -doublet transitions are fast compared to rotational transitions.

Quantum scattering calculations on the OH-Ar and OH-He systems have recently been carried out by Werner and co-workers.⁶ The OH-Ar calculations are based on an *ab initio* potential that was used also for the calculations of the bound energy states of the OH-Ar van der Waals complex.⁷ For OH-He an *ab initio* potential was derived by Vegiri and Farantos.⁸ Because of its importance for chemical kinetics and temperature measurements in combustion processes, rotational relaxation rates in the $A^2\Sigma^+$ state of OH were calculated by Jörg *et al.* for OH-He (Refs. 9 and 10) and by Degli-Esposti and Werner for the system OH-Ar.¹¹

In this study we present the results of a molecular beam experiment in which the OH radical is prepared in two ways. One in which only the upper parity substate of the $X^2\Pi_{3/2}$, $J=\frac{3}{2}$ Λ -doublet is populated and another one in which both substates are populated. A setup of two crossed pulsed molecular beams is used, and, in the case of single state preparation, a hexapole electrostatic state selector. Final state detection is performed by electronic laser-induced fluorescence (LIF) spectroscopy on the OH radical. Parity resolved relative state-to-state cross sections are derived from the measurements for transitions out of both the $J=\frac{3}{2}^+$ state and the $J=\frac{3}{2}^-$ state. The collision energy of 394 and 451 cm^{-1} for He and Ar, respectively, enables determination of the cross sections for transitions to states with J up to $\frac{9}{2}$ in $\Pi_{3/2}(F_1)$ and J up to $\frac{5}{2}$ in $\Pi_{1/2}(F_2)$. For convenience an energy level scheme of these states with their parities and symmetries is given in Fig. 1. Our experimental results are compared with the theoretical cross sections of Werner *et al.*⁶ and show good agreement in most cases.

II. EXPERIMENT

A. Experimental setup

In the present scattering experiment use is made of a crossed molecular beam setup. The molecular beam machine has been described in full detail in previous publications.^{13,14} Two pulsed molecular beams are crossed at right angles, using modified Bosch-type fuel injectors with a pulse width [full-width at half-maximum (FWHM)] of ~ 1 ms. The primary beam contains the OH radicals which are rotationally excited by collisions with secondary beam targets He or Ar. The OH radicals are produced in an

FIG. 1. Energy level diagram of the OH $^2\Pi$ electronic ground state. The energy levels are labeled with their rotational quantum number J , parity p , and Λ -doubling symmetry e/f . The energy difference between the components of each Λ -doublet is exaggerated for reasons of clarity.

electrical discharge just downstream the primary valve exit hole, as is illustrated in Fig. 2. For this purpose an 18 Torr H_2O in Ar mixture is expanded into vacuum at a total backing pressure of 1.5 atm. A small electrode ring is positioned 3 mm downstream the nozzle exit hole. The ring is 6 mm in diameter and is made of 1 mm thick stainless steel. A negative high voltage of typically 4–5 kV is applied to the electrode and as soon as the expansion takes place a discharge occurs between the electrode and the pulsed valve, which is on earth potential. In the expansion the water molecules dissociate and the OH radicals are produced very efficiently. After the expansion the OH molecular pulse is shaped into a primary beam by a 5 mm skimmer ~ 20 mm downstream from the nozzle orifice.

In the case of single state preparation an electrostatic state selector is positioned ~ 20 mm behind the skimmer. Use is made of a hexapole which acts as an electrostatic positive lens for molecules in an antisymmetric (f) Λ -doublet state and as a negative lens for molecules being in a symmetric (e) Λ -doublet state. The state selector is 230 mm long and consists of six 2 mm diam rods at a

FIG. 2. Discharge radical source. A high voltage is applied to an electrode ring underneath the pulsed valve exit hole. During the expansion a discharge occurs between valve and electrode in which radicals are produced.

distance of 2 mm from each other. The hexapole is operated at voltages up to 30 kV, well below electrical breakdown. The focus of the state selector occurs ~ 40 mm behind the exit opening of the hexapole and coincides with the scattering volume and detection region. In the discharge producing the OH radicals also ions and electrons are produced inside the molecular beam, which give rise to an electrical current of several 100 μA through the hexapole rods. Since the high voltage power supply for the state selector is not able to accept these high currents, a diaphragm, with an opening of 6 mm in diameter, is positioned between the primary beam skimmer and the hexapole. Putting the diaphragm on earth potential and applying a voltage of typically 100 V to the skimmer results in an efficient shielding of the hexapole from incoming ions or electrons. Consequently the current through the hexapole device is reduced to 10 μA or less, yielding a stable high voltage output and constant focusing efficiency.

In the case of preparation of both $J=\frac{3}{2}$ Λ -doublet states, no use is made of the hexapole. Instead, a second skimmer is mounted just in front of the scattering region to shape the beam in a homogeneous flux of particles. The total distance between the nozzle and the scattering region is then ~ 15 cm.

The secondary beam is produced in a differentially pumped vacuum chamber, separated from the scattering chamber by a 5 mm skimmer. As a result the scattering region is geometrically confined to within a volume of about $8 \times 8 \times 8 \text{ mm}^3$. During operation of both molecular beam valves the pressure inside the vacuum chamber does not exceed 10^{-5} Torr. We measured the velocity of the primary and secondary beams by means of a fast ionization gauge positioned on the beam axis. By varying the distance from the nozzle to the ionization gauge and measuring the corresponding flight times we estimated the velocities to be $v_{\text{OH}} = 670 \text{ ms}^{-1}$ and for the secondary beam $v_{\text{He}} = 1560 \text{ ms}^{-1}$ and $v_{\text{Ar}} = 670 \text{ ms}^{-1}$. Knowing the beam velocities it is possible to calculate the center-of-mass collision energies involved in the scattering events, $E_{\text{coll}}(\text{OH-He}) = 394 \text{ cm}^{-1}$ and $E_{\text{coll}}(\text{OH-Ar}) = 451 \text{ cm}^{-1}$.

Before and after the collision process the rotational state distribution of the OH radicals is probed state selectively by means of LIF spectroscopy of the $A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi_i (v''=0)$ electronic transition at 308 nm. For this purpose the frequency doubled output of a XeCl excimer laser pumped dye laser is guided into the scattering region. The dye laser operates at Rhodamine-B dye, lasing between 600 and 640 nm. The output of the dye laser is frequency doubled in a KDP crystal yielding tunable ultraviolet (UV) radiation in the 308 nm wavelength region with a bandwidth of $\approx 0.4 \text{ cm}^{-1}$. The output power is typically 3 mJ/15 ns pulse, which is large enough to cause complete saturation of all transitions involved in this experiment. The wings of the laser beam, where the power density may be too low to saturate the transitions, are cut off using a diaphragm.

Following the general selection rules for a $2\Sigma^+ \leftarrow 2\Pi_i$ electronic transition, OH molecules in the upper Λ -doublet states are probed by the Q_1 and P_2 rotational

FIG. 3. Boltzmann plot showing the rotational population distribution of the electronic ground state OH, directly after the expansion without electrostatic state selection. A rotational temperature of ≈ 35 K can be associated with the lowest rotational states. For higher J -values the rotational cooling is less efficient, resulting in a nonthermal Boltzmann distribution.

transitions, while molecules in the lower Λ -doublet states are probed by the Q_2 and P_1 transitions. The resulting LIF signal is imaged onto the first cathode plate of a photon multiplier tube by means of collecting optics using a spatial filtering diaphragm. A Schott color filter (UG11) in front of the photon multiplier is used to suppress stray light and scattered light arising from the discharge. The resulting signal is then processed by a boxcar averager and directed to a strip-chart recorder and AT computer. Simultaneously the UV power is monitored by means of a photodiode.

B. Initial state distribution

Initial state preparation of the OH radicals is achieved by the supersonic expansion of the OH molecular pulse, eventually followed by electrostatic state selection in the hexapole electric field. During the expansion rotational and vibrational energy of the radical is converted into translational energy which results in cooling of the internal degrees of freedom of the OH radicals. In Fig. 3 a Boltzmann plot is shown of the rotational state distribution in the $X^2\Pi_{3/2}(F_1)$ and $X^2\Pi_{1/2}(F_2)$ states of OH in the case where the hexapole state selector was removed. About 94% of the OH electronic ground state population is contained in the lowest rotational state $J=\frac{3}{2}$ of the F_1 state. The rest of the population is distributed among the higher rotational states and the F_2 spin-orbit multiplet of OH. About 3.5% of the population is contained in the $J=\frac{5}{2}$ state of the F_1 multiplet. Although the Boltzmann plot indicates a nonthermal behavior of the population distribution in the higher rotational states, an effective rotational temperature can be ascribed to the two lowest rotational states of the F_1 state, yielding $T_{\text{rot}} \approx 35$ K. The energy difference between the two Λ -doublet components is only 0.05 cm^{-1} for the $J=\frac{3}{2}$ rotational state in the F_1 state. One should therefore expect that both $J=\frac{3}{2}$ Λ -doublet substates are almost equally populated in the supersonic expansion. However, when they are measured by the $Q_1(1)$ and the $P_1(1)$ lines, they turn out to have a remarkably large population difference with a ratio of 100:68.

In order to be sure that no error was made due to the partial overlap of the $Q_1(1)$ and the $Q_{21}(1)$ lines we repeated the measurements of the population distribution at

FIG. 4. Spectrum showing the $Q_1(1)$ and the $P_1(1)$ lines as probed by the PDA system. Indicated are the underlying hyperfine transitions, $F' - F''$, which are partly resolved. The frequency scale is only indicative. The separation of the two hyperfine components of the $P_1(1)$ line is 0.024 cm^{-1} .

higher resolution. Hereto a combination of a single mode ring dye laser and a Nd:YAG pumped pulsed dye amplifier was applied.¹² With a Fourier limited linewidth of 150 MHz for the frequency doubled radiation, and at nonsaturating conditions, spectra for the $Q_1(1)$ and $P_1(1)$ transitions were obtained as shown in Fig. 4. The intensity ratios of the hyperfine components correspond exactly to the expected ratios for nonsaturated excitation. From the intensity ratio between the $P_1(1)$ and the $Q_1(1)$ lines the same factor of 0.68 was obtained for the population ratio between the lower and the upper $J=\frac{3}{2}$ Λ -doublet state as was derived from the low resolution measurements. We have no definitive explanation for this high degree of inversion of the $J=\frac{3}{2}$ Λ -doublet population, considering the relatively large thermalizing collision rate between the Λ -doublet levels of OH by seeding gas Ar (see later). It is probably due to a strong nonthermal population distribution of OH in the production from H_2O in the discharge.

If use is made of the hexapole, the upper component ($\frac{3}{2}^+$) of the $|X^2\Pi_{3/2}, J=\frac{3}{2}\rangle$ Λ -doublet is focused towards the beam axis, while the other component is defocused. In Fig. 5 the focusing efficiency of the hexapole state selector is illustrated. The $Q_1(1)$ and $P_1(1)$ LIF signals are given as a function of the high voltage applied to the hexapole rods. The high voltage was limited to a maximum value of 30 kV in order to avoid electrical breakdown. From the figure it follows that the focusing efficiency for the $\frac{3}{2}^+$ state, probed

FIG. 5. Diagram showing the focusing efficiency of the hexapole state selector for the $F_1, J^P=\frac{3}{2}^+$ state [probed by the $Q_1(1)$ transition], and the $F_1, J^P=\frac{3}{2}^-$ state [probed by the $P_1(1)$ transition]. At a voltage of 30 kV the separation factor of both Λ -doublet states is ≈ 30 .

by the $Q_1(1)$ transition, reaches a value of ≈ 8 at a maximum voltage of 30 kV. At this voltage the $\frac{3}{2}^-$ state density, given by the $P_1(1)$ signal, is decreased by a factor of ≈ 4 . The net effect of the electrostatic state selection is an overpopulation of the $J=\frac{3}{2}$ positive parity component by a factor of 30 with respect to the $J=\frac{3}{2}$ negative parity component. With regard to the experimental accuracy of $\approx 10\%$ the initial parity substate preparation can be considered adequate for performing a real state-to-state collision experiment. However, since the $J^P=\frac{5}{2}^-$ state is also affected by the electrostatic state selection process, its initial population increases as a function of state selector voltage. At a voltage of 30 kV the population of the $J^P=\frac{5}{2}^-$ state is equal to 7.0% of the $J^P=\frac{3}{2}^+$ state population. Consequently, when we neglect all the other states, the measured cross section $\sigma(i \rightarrow f)$ is made up of two contributions,

$$\sigma(i \rightarrow f) = 0.935 \cdot \sigma(F_{1, \frac{3}{2}^+} \rightarrow f) + 0.065 \cdot \sigma(F_{1, \frac{5}{2}^-} \rightarrow f). \quad (1)$$

A similar correction should be made for the collisional excitation of the $F_{1, \frac{5}{2}^-}$ state. Since any scattering out of this 6.5% initially prepared state results in a decrease of the scattering signal, the measured cross section for collisional excitation into this state is equal to

$$\begin{aligned} \sigma(i \rightarrow F_{1, \frac{5}{2}^-}) &= 0.935 \cdot \sigma(F_{1, \frac{3}{2}^+} \rightarrow F_{1, \frac{5}{2}^-}) \\ &\quad - 0.065 \sum_j' \sigma(F_{1, \frac{5}{2}^-} \rightarrow j), \end{aligned} \quad (2)$$

where the summation in the last equation is equal to the total inelastic cross section of the $F_{1, J^P=\frac{5}{2}^-}$ state.

If no use is made of the hexapole similar equations as above hold for the cross sections, yielding

$$\begin{aligned} \sigma(i \rightarrow f) &= 0.574 \cdot \sigma(F_{1, \frac{3}{2}^+} \rightarrow f) + 0.388 \cdot \sigma(F_{1, \frac{3}{2}^-} \rightarrow f) \\ &\quad + 0.022 \cdot \sigma(F_{1, \frac{5}{2}^-} \rightarrow f) + 0.016 \cdot \sigma(F_{1, \frac{5}{2}^+} \rightarrow f) \end{aligned} \quad (3)$$

and for the measured cross sections for transitions to the $\frac{5}{2}^+$ and $\frac{5}{2}^-$ states,

$$\begin{aligned} \sigma(i \rightarrow F_{1, \frac{5}{2}^-}) &= 0.583 \cdot \sigma(F_{1, \frac{3}{2}^+} \rightarrow F_{1, \frac{5}{2}^-}) \\ &\quad + 0.394 \cdot \sigma(F_{1, \frac{3}{2}^-} \rightarrow F_{1, \frac{5}{2}^-}) \\ &\quad - 0.022 \sum_j' \sigma(F_{1, \frac{5}{2}^-} \rightarrow j), \end{aligned} \quad (4)$$

$$\begin{aligned} \sigma(i \rightarrow F_{1, \frac{5}{2}^+}) &= 0.587 \cdot \sigma(F_{1, \frac{3}{2}^+} \rightarrow F_{1, \frac{5}{2}^+}) \\ &\quad + 0.397 \cdot \sigma(F_{1, \frac{3}{2}^-} \rightarrow F_{1, \frac{5}{2}^+}) \\ &\quad - 0.016 \sum_j' \sigma(F_{1, \frac{5}{2}^+} \rightarrow j). \end{aligned} \quad (5)$$

III. RESULTS AND INTERPRETATION

As shown in Ref. 13 the state-to-state collision cross section $\sigma(i \rightarrow f)$ for scattering out of the initially prepared state $|i\rangle$ into a final state $|f\rangle$ can be extracted from the scattering spectra in a rather straightforward manner if single collision conditions are fulfilled. The final state in the scattering process $|f\rangle$ is probed by a rotational transition $|f\rangle \rightarrow |f'\rangle$ in the electronic $A \leftarrow X$ band, giving a LIF signal $S_{ff'}$. The scattering signal $\delta S_{ff'}$ represents the change in signal $S_{ff'}$ upon collisions with the secondary beam molecules. From these scattering signals $\delta S_{ff'}$ the relative cross sections $\sigma(i \rightarrow f)$ are deduced via the following formula:

$$\sigma(i \rightarrow f) \propto \frac{\delta S_{ff'}}{n(i) \cdot \mathcal{L}_{ff'} \cdot P_{ff'} \cdot F}. \quad (6)$$

In this formula $\mathcal{L}_{ff'}$ represents the rotational line strength of the transition, $P_{ff'}$ is the laser power at the specific transition frequency and F represents the flux-density transformation relating the particle densities measured with the incoming and scattered particle fluxes.¹⁵ This transformation F contains the particle velocity and consequently its value depends on the scattered state $|f\rangle$ of the OH radical. However, since the laboratory velocity of the OH molecules is mainly determined by the center-of-mass velocity, which does not change during the collision, the outcome of the flux-density transformation is nearly the same for all $|f\rangle$ states probed. In their paper on the CH-He collision experiment MacDonald and Liu² showed that as long as single collision conditions are fulfilled and all the scattered molecules can be detected regardless of their final velocity, i.e., before they leave the detection region, the LIF detection technique can be used as a monitor for beam fluxes instead of beam densities. Our experimental conditions with respect to beam geometries and beam velocities fulfill the conditions required for this flux probe and consequently the factor F will have nearly the same value for all final states $|f\rangle$. Since we are studying relative integral cross sections the factor F can be omitted from Eq. (6).

The relation between the relative cross section $\sigma(i \rightarrow f)$ and the scattering signal $\delta S_{ff'}$, as expressed in Eq. (6), is valid only if single collision conditions are obeyed.¹³ Careful checks have been performed in order to make sure that collisional effects are linear with secondary beam density. Scattering spectra were recorded at different backing pressures of the secondary beam. For low pressures the intensities of the spectral lines show a linear dependence on the backing pressure. However, above a certain critical value for the secondary beam stagnation pressure the scattering spectra show different relative line intensities compared to the low pressure spectra, indicating that higher order collision processes come into play.¹³ Under these circumstances the relation between the scattering signal $\delta S_{ff'}$ and the cross sections becomes too complex to derive a state-to-state cross section $\sigma(i \rightarrow f)$ from the scattering spectra. In order to avoid these secondary or higher order collisions

the secondary beam backing pressure was kept below 400 Torr for both scattering partners He and Ar.

The state-to-state cross sections reported here are obtained by probing the rotational population distribution by means of the Q_1 , P_1 , Q_2 , and P_2 branches in the $A^2\Sigma^+$, $v'=0 \leftarrow X^2\Pi_i$, $v''=0$ band of OH. The laser power of typically 3 mJ/15 ns was enough to saturate these strong transitions. Since we are determining only relative cross sections the line strength $\mathcal{L}_{ff'}$ and laser power $P_{ff'}$ in Eq. (6) can be omitted.

In their paper about collisions between OH and H₂ (Ref. 1) Andresen *et al.* argued that a P transition cannot couple all the substrates m_J of a rotational level in the lower electronic state to the upper one due to a vanishing matrix element for $\Delta m_J \neq 0$. In the saturation limit this would result in a lower excitation rate for P transitions compared to R and Q transitions. However, this holds only if the laser is purely linearly polarized and if no other disturbing fields (e.g., the earth's magnetic field) are present. In practice this situation is unlikely to occur. In our case we measured the same intensities for the $P_1(1)$, the $R_1(1)$ and the $R_1(1)'$ lines, indicating that both the saturation conditions are fulfilled and the population distribution can be probed reliably by P transitions. A similar comparison of the $P_1(2)$ and the $R_1(2)$ lines led to the same conclusion.

For scattering in the F_1 spin-orbit multiplet ($F_1 \rightarrow F_1$) cross sections could be determined for J' -values up to $\frac{9}{2}$, whereas for the spin-orbit multiplet changing $F_1 \rightarrow F_2$ transition excitations into rotational states up to $J' = \frac{5}{2}$ were measured. Due to coinciding $Q_2(2)$ and $Q_2(3)$ lines in the LIF spectra the scattering signal measured at these transitions in fact represents the sum cross section $\sigma(i \rightarrow F_{2,\frac{3}{2}}^-) + \sigma(i \rightarrow F_{2,\frac{5}{2}}^+)$.

The data were obtained by averaging the results from several (5 to 10 per rotational state) scattering measurements. Each measurement was constructed from more than 2000 pulses both with collisions and without collisions while the laser frequency was kept fixed at resonance. A rather large experimental error for some cross sections resulted from a poor signal to noise ratio for the corresponding lines in the LIF scattering spectra. When the decrease of population in the initially prepared state(s) was compared with the sum of populations scattered into all other rotational states, this balance showed, within the experimental accuracy, a canceling of the collisionally excited population by the decrease of the population of the initially prepared state. As a result we may conclude that elastic scattering effects are not detected; as many molecules in the initial state(s) are scattered out of the probe region as there are scattered into this area.

In Table I the relative state-to-state cross sections $\sigma(i \rightarrow f)$ for scattering out of the $\frac{3}{2}^+$ state as defined by Eq. (1) and obtained from Eq. (6), are given for the collision partner He. The same is done in Table II for OH-Ar scattering. The values for scattering into the F_1 , $J' = \frac{5}{2}^-$ state have been corrected for the scattering out of this 6.5% initially populated state according to Eq. (2). Hereto we calculated the out-scattering using the theoretical value for

TABLE I. Relative state-to-state cross sections $0.935 \cdot \sigma(^2\Pi_{3/2,2}^{3+}, f \rightarrow ^2\Pi_{\Omega';J''P'}, \epsilon') + 0.065 \cdot \sigma(^2\Pi_{3/2,2}^{5-}, f \rightarrow ^2\Pi_{\Omega';J''P'}, \epsilon')$ for rotational excitation of ground state OH by collisions with He at a collision energy of 394 cm^{-1} . The experimental data are scaled to have the same total cross section as predicted by the theory. The theoretical data are from Werner *et al.* (Ref. 6) and represent absolute cross sections. All values are in $\text{\AA}^2$.

$^2\Pi_{3/2} \rightarrow ^2\Pi_{3/2}$				$^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$			
J'	$\epsilon'(p')$	Experiment	Theory	J'	$\epsilon'(p')$	Experiment	Theory
$\frac{5}{2}$	$f(-)$	0.53 ± 0.07	0.316	$\frac{1}{2}$	$f(-)$	0.09 ± 0.03	0.105
$\frac{7}{2}$	$f(+)$	0.23 ± 0.03	0.131	$\frac{3}{2}$	$f(+)$	0.95 ± 0.11	1.360
$\frac{9}{2}$	$f(-)$	0.03 ± 0.01	0.002	$\frac{5}{2}$	$f(-)$	0.10 ± 0.04	0.082
$\frac{3}{2}$	$e(-)$	0.84 ± 0.06	0.574	$\frac{1}{2}$	$e(+)$	2.75 ± 0.10	2.866
$\frac{5}{2}$	$e(+)$	3.91 ± 0.13	4.484	$\frac{3}{2}$	$e(-)$	0.24 ± 0.08	0.281
$\frac{7}{2}$	$e(-)$	0.85 ± 0.07	0.481	$\frac{5}{2}$	$e(+)$		
$\frac{9}{2}$	$e(+)$	0.19 ± 0.02	0.030				

the ratio of the total inelastic cross sections of the $\frac{3}{2}^+$ and the $\frac{5}{2}^-$ states. Since the initial population in the $F_{1, \frac{3}{2}^+}$ state with respect to the $F_{1, \frac{5}{2}^-}$ state is well known, the scattering out of the $\frac{5}{2}^-$ state relative to the scattering out of the $F_{1, \frac{3}{2}^+}$ state can be derived. In the tables also the theoretical values for these cross sections as obtained by Werner and co-workers⁶ are given. The experimental values are normalized with respect to the theoretical values by equalizing the sum of the cross sections.

In the Tables III and IV the cross sections for scattering out of the $\frac{3}{2}^-$ state are given for, respectively, He and Ar. These values were constructed using the results of the measurements with and without state selector via the following procedure. The measured values for scattering into the $F_{1, \frac{5}{2}^-}$ and the $F_{1, \frac{5}{2}^+}$ states were first corrected for the scattering out of these initially slightly populated states. This was done in the same way as described above but now using Eqs. (4) and (5). Then the out-scattering of the $\frac{3}{2}^+$ and $\frac{3}{2}^-$ states was corrected for mutual in-scattering, which

TABLE II. Relative state-to-state cross sections $0.935 \cdot \sigma(^2\Pi_{3/2,2}^{3+}, f \rightarrow ^2\Pi_{\Omega';J''P'}, \epsilon') + 0.065 \cdot \sigma(^2\Pi_{3/2,2}^{5-}, f \rightarrow ^2\Pi_{\Omega';J''P'}, \epsilon')$ for rotational excitation of ground state OH by collisions with Ar at a collision energy of 451 cm^{-1} . The experimental data are scaled to have the same total cross section as predicted by the theory. The theoretical data are from Werner *et al.* (Ref. 6) and represent absolute cross sections. All values are in $\text{\AA}^2$.

$^2\Pi_{3/2} \rightarrow ^2\Pi_{3/2}$				$^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$			
J'	$\epsilon'(p')$	Experiment	Theory	J'	$\epsilon'(p')$	Experiment	Theory
$\frac{5}{2}$	$f(-)$	2.23 ± 0.65	1.088	$\frac{1}{2}$	$f(-)$	0.18 ± 0.18	0.302
$\frac{7}{2}$	$f(+)$	0.29 ± 0.17	0.122	$\frac{3}{2}$	$f(+)$	0.28 ± 0.12	0.560
$\frac{9}{2}$	$f(-)$	0.14 ± 0.14	0.003	$\frac{5}{2}$	$f(-)$	0.16 ± 0.12	0.278
$\frac{3}{2}$	$e(-)$	14.88 ± 1.36	12.495	$\frac{1}{2}$	$e(+)$	1.57 ± 0.32	1.866
$\frac{5}{2}$	$e(+)$	9.22 ± 0.91	11.718	$\frac{3}{2}$	$e(-)$	0.49 ± 0.11	0.490
$\frac{7}{2}$	$e(-)$	0.98 ± 0.27	1.875	$\frac{5}{2}$	$e(+)$		
$\frac{9}{2}$	$e(+)$	0.66 ± 0.34	0.279				

TABLE III. Relative state-to-state cross sections $0.962 \cdot \sigma(^2\Pi_{3/2,2}^{3+}, e \rightarrow ^2\Pi_{\Omega';J''P'}, \epsilon') + 0.038 \cdot \sigma(^2\Pi_{3/2,2}^{5+}, e \rightarrow ^2\Pi_{\Omega';J''P'}, \epsilon')$ for rotational excitation of ground state OH by collisions with He at a collision energy of 394 cm^{-1} . The experimental data are scaled to have the same total cross section as predicted by the theory. The theoretical data are from Werner *et al.* (Ref. 6) and represent absolute cross sections. All values are in $\text{\AA}^2$.

$^2\Pi_{3/2} \rightarrow ^2\Pi_{3/2}$				$^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$			
J'	$\epsilon'(p')$	Experiment	Theory	J'	$\epsilon'(p')$	Experiment	Theory
$\frac{5}{2}$	$f(-)$	0.85 ± 0.09	0.370	$\frac{1}{2}$	$f(-)$	1.68 ± 0.09	2.033
$\frac{7}{2}$	$f(+)$	0.08 ± 0.03	0.076	$\frac{3}{2}$	$f(+)$	0.44 ± 0.11	0.097
$\frac{9}{2}$	$f(-)$	0.02 ± 0.02	0.002	$\frac{5}{2}$	$f(-)$	0.30 ± 0.04	0.203
$\frac{5}{2}$	$e(+)$	< 0.28	0.862	$\frac{1}{2}$	$e(+)$	0.49 ± 0.16	0.035
$\frac{7}{2}$	$e(-)$	0.55 ± 0.09	0.900	$\frac{3}{2}$	$e(-)$	1.20 ± 0.10	1.065
$\frac{9}{2}$	$e(+)$	0.06 ± 0.03	0.028	$\frac{5}{2}$	$e(+)$		

does not cancel because of the different initial populations. This could be done using the experimental values for the cross section $\frac{3}{2}^+ \rightarrow \frac{3}{2}^-$ and the ratio of the initial populations. Then the experimental values for the cross sections as obtained with the hexapole were scaled to have the same total cross section as the out-scattering of the $\frac{3}{2}^+$ state. These values were then subtracted from the values obtained without hexapole yielding the cross sections for the $\frac{3}{2}^-$ state. The values presented in the table are scaled to have the same total cross section as the theoretical values. The experimental error is rather large due to the subtraction procedure.

It must be noted that the correction to the $J=\frac{5}{2}$ state had not been taken into account by Andresen *et al.*¹ in a similar OH-H₂ crossed beam experiment. In their experiment the $J=\frac{5}{2}$ state was occupied for $\sim 10\%$ and a considerable amount of out-scattering must have taken place.

IV. DISCUSSION

A. Cross sections for the $\frac{3}{2}^+$ state

In Figs. 6 and 7 the cross sections from Tables I and II are presented graphically for the OH-He and OH-Ar scattering, respectively. The relative cross section is given as a

TABLE IV. Relative state-to-state cross sections $0.962 \cdot \sigma(^2\Pi_{3/2,2}^{3-}, e \rightarrow ^2\Pi_{\Omega';J''P'}, \epsilon') + 0.038 \cdot \sigma(^2\Pi_{3/2,2}^{5+}, e \rightarrow ^2\Pi_{\Omega';J''P'}, \epsilon')$ for rotational excitation of ground state OH by collisions with Ar at a collision energy of 451 cm^{-1} . The experimental data are scaled to have the same total cross section as predicted by the theory. The theoretical data are from Werner *et al.* (Ref. 6) and represent absolute cross sections. All values are in $\text{\AA}^2$.

$^2\Pi_{3/2} \rightarrow ^2\Pi_{3/2}$				$^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$			
J'	$\epsilon'(p')$	Experiment	Theory	J'	$\epsilon'(p')$	Experiment	Theory
$\frac{5}{2}$	$f(-)$	3.16 ± 0.54	3.139	$\frac{1}{2}$	$f(-)$	0.80 ± 0.16	0.389
$\frac{7}{2}$	$f(+)$	0.27 ± 0.12	0.165	$\frac{3}{2}$	$f(+)$	0.51 ± 0.13	0.050
$\frac{9}{2}$	$f(-)$	< 0.13	0.002	$\frac{5}{2}$	$f(-)$	0.27 ± 0.10	0.276
$\frac{5}{2}$	$e(+)$	1.77 ± 0.85	1.803	$\frac{1}{2}$	$e(+)$	0.60 ± 0.26	0.084
$\frac{7}{2}$	$e(-)$	1.98 ± 0.32	2.197	$\frac{3}{2}$	$e(-)$	0.22 ± 0.10	1.131
$\frac{9}{2}$	$e(+)$	< 0.31	0.343	$\frac{5}{2}$	$e(+)$

FIG. 6. Relative state-to-state cross sections $0.935 \cdot \sigma(^2\Pi_{3/2, 3/2^+}, f \rightarrow ^2\Pi_{\Omega', J'^{p'}, \epsilon'}) + 0.065 \cdot \sigma(^2\Pi_{3/2, 5/2^-}, f \rightarrow ^2\Pi_{\Omega', J'^{p'}, \epsilon'})$ for OH-He scattering. The top part of the figure shows the cross sections for multiplet conserving transitions ($\Pi_{3/2} \rightarrow \Pi_{3/2}$); the lower part gives the multiplet changing transitions. The data indicated by the squares represent the cross sections for symmetry conserving rotational excitation. The circles show the cross sections for symmetry changing collisional excitation. The experimental error is indicated by the error bars. The theoretical values from Ref. 6 are represented by the open squares and circles.

function of final angular momentum J' , parity p' and Λ -doublet symmetry ϵ' . With the exception of the $F_1, J = \frac{3}{2}$ Λ -doublet transition, the overall behavior of the cross sections looks very similar for OH-Ar and OH-He scattering. For both collision partners a symmetry propensity rule shows up. For spin-orbit conserving as well as for

spin-orbit changing transitions the symmetry changing $f \rightarrow e$ rotational excitations are preferred over the symmetry conserving transitions. This propensity is, however, not observed for the excitation into the $F_2, J = \frac{3}{2}$ state. For OH-He scattering the cross sections for spin-orbit changing transitions ($F_1 \rightarrow F_2$) are of the same order of magnitude as those for scattering in the F_1 spin-orbit manifold. This is in agreement with the relaxation measurements of Crosley *et al.*⁵ For OH-Ar scattering the spin-orbit conserving $F_1 \rightarrow F_1$ rotational excitations are almost an order of magnitude stronger than the spin-orbit changing $F_1 \rightarrow F_2$ transitions.

In their quantum scattering calculations Werner *et al.*⁶ used an OH-Ar *ab initio* potential that was used also for the calculations of the bound energy states of the OH-Ar van der Waals complex.⁷ For OH-He the *ab initio* potential derived by Degli-Esposti⁹ was applied. The scattering calculations were performed at our experimental collision energies of 394 and 451 cm^{-1} for OH-He and OH-Ar scattering, respectively.

Comparison of their data with our experimental cross sections shows a good agreement. The same overall behavior of experimental and calculated cross sections as a function of J' is obtained as can be seen from Figs. 6 and 7. For OH-He scattering both theory and experiment predict that the $F_1 \rightarrow F_1$ transitions are comparable in strength with the spin-orbit changing $F_1 \rightarrow F_2$ transitions. Furthermore the experimentally observed propensity for symmetry changing $F_1 \rightarrow F_1$ transitions is confirmed by theory as well. For the spin-orbit changing $F_1 \rightarrow F_2$ transitions this propensity rule is no longer predicted by theory for all transitions as observed in the experiment. Remarkable is the very weak $F_1, J = \frac{3}{2}$ Λ -doublet transition for OH-He scattering, as observed in the experiment.

Also for the OH-Ar collision system theory is in good agreement with experiment. Figure 7 shows the collision cross sections for OH-Ar scattering and the first thing to notice is that the $F_1, J = \frac{3}{2}$ Λ -doublet transition is more than an order of magnitude stronger than for He scattering. In general the cross sections for spin-orbit conserving $F_1 \rightarrow F_1$ transitions are stronger than the ones for the $F_1 \rightarrow F_2$ excitations in contrast to OH-He scattering.

The calculated contribution of the 6.5% populated $\frac{5}{2}^-$ state to the experimental cross section (1) is $\sim 6.5\%$ or smaller for most of the transitions. However, in case of the spin-orbit changing collisions to the $F_2, J^p = \frac{1}{2}^-$ and $J^p = \frac{3}{2}^-$ states the cross sections are strongly determined by transitions from the $F_2, J^p = \frac{5}{2}^-$ state. This conceals the strong propensity for transitions to these states out of the $F_1, J^p = \frac{3}{2}^+$ state as predicted by theory. For He scattering the theoretical cross sections for the $F_1, J^p = \frac{3}{2}^+ \rightarrow F_2, J^p = \frac{1}{2}^+$ and $J^p = \frac{1}{2}^-$ transitions are 3.064 and 0.009 $\text{\AA}^2$, respectively, showing a near parity selection rule. Since the cross section for the $F_1, J^p = \frac{5}{2}^- \rightarrow F_2, J^p = \frac{1}{2}^-$ transition is calculated to be 1.492 $\text{\AA}^2$ a sizable collision induced population is measured in the $F_2, J^p = \frac{1}{2}^-$ state. A similar situation is present for the excitation to the $F_2, J^p = \frac{3}{2}^-$ state. Also for Ar scattering the efficient excitation from the $F_1, J^p = \frac{5}{2}^-$ state to the $F_2, J^p = \frac{1}{2}^-$ state prevents us

FIG. 7. Relative state-to-state cross sections $0.935 \cdot \sigma(^2\Pi_{3/2, 3/2^+}, f \rightarrow ^2\Pi_{\Omega', J'^{p'}, \epsilon'}) + 0.065 \cdot \sigma(^2\Pi_{3/2, 5/2^-}, f \rightarrow ^2\Pi_{\Omega', J'^{p'}, \epsilon'})$ for OH-Ar scattering. The top part of the figure shows the cross sections for multiplet conserving transitions ($\Pi_{3/2} \rightarrow \Pi_{3/2}$); the lower part gives the multiplet changing transitions. The data indicated by the squares represent the cross sections for symmetry conserving rotational excitation. The circles show the cross sections for symmetry changing collisional excitation. The experimental error is indicated by the error bars. The theoretical values from Ref. 6 are represented by the open squares and circles.

FIG. 8. Relative state-to-state cross sections $0.962 \cdot \sigma(^2\Pi_{3/2,3/2}, e \rightarrow ^2\Pi_{\Omega', J''P'}, \epsilon') + 0.038 \cdot \sigma(^2\Pi_{3/2,3/2}, f \rightarrow ^2\Pi_{\Omega', J''P'}, \epsilon')$ for OH-He scattering. The top part of the figure shows the cross sections for multiplet conserving transitions ($\Pi_{3/2} \rightarrow \Pi_{3/2}$); the lower part gives the multiplet changing transitions. The data indicated by the squares represent the cross sections for symmetry changing rotational excitation. The circles show the cross sections for symmetry conserving collisional excitation. The experimental error is indicated by the error bars. The theoretical values from Ref. 6 are represented by the open squares and circles.

FIG. 9. Relative state-to-state cross sections $0.962 \cdot \sigma(^2\Pi_{3/2,3/2}, e \rightarrow ^2\Pi_{\Omega', J''P'}, \epsilon') + 0.038 \cdot \sigma(^2\Pi_{3/2,3/2}, f \rightarrow ^2\Pi_{\Omega', J''P'}, \epsilon')$ for OH-Ar scattering. The top part of the figure shows the cross sections for multiplet conserving transitions ($\Pi_{3/2} \rightarrow \Pi_{3/2}$); the lower part gives the multiplet changing transitions. The data indicated by the squares represent the cross sections for symmetry changing rotational excitation. The circles show the cross sections for symmetry conserving collisional excitation. The experimental error is indicated by the error bars. The theoretical values from Ref. 6 are represented by the open squares and circles.

from observing a near parity selection rule for the weakly populated $F_1, J^P = \frac{3}{2}^+ \rightarrow F_2, J^P = \frac{1}{2}^\pm$ transitions as predicted by theory.

B. Cross sections for the $\frac{3}{2}^-$ state

The results for the cross sections for the $\frac{3}{2}^-$ state are presented graphically in Figs. 8 and 9. With respect to the $F_1 \rightarrow F_1$ transitions the overall behavior observed for He collisions is the same as for Ar collisions. However, when compared to the scattering out of the $\frac{3}{2}^+$ state a remarkable difference shows up; there is no propensity rule with respect to the symmetry. In particular for transitions to the $J^P = \frac{7}{2}^\pm$ states a clear preference for conservation of the symmetry is observed instead of a symmetry change. This is also what theory predicts for both Ar and He collisions. For Ar a nearly perfect agreement is obtained as can be seen from the upper part of Fig. 9. In the case of He, however, a large deviation between the calculated and experimental cross sections for the transitions to the $J^P = \frac{5}{2}^\pm$ is present; instead of a symmetry change, the theory predicts a preference for conservation of the symmetry, contrary to the Ar collisions.

For the spin-orbit changing collisions ($F_1 \rightarrow F_2$) the overall dependence of the cross sections on J' is similar to the scattering of OH in $J^P = \frac{3}{2}^+$, at least for the case of He. We observe a clear preference for a change of symmetry in transitions to $J^P = \frac{1}{2}^\pm$, whereas transitions to $J^P = \frac{3}{2}^\pm$ tend to conserve the symmetry. This is also in agreement with the theory. For Ar collisions, strong deviations seem to be present. It must be noted, however, that the cross sections are quite small, making deviations between theory and experiment easily visible on this scale. Nevertheless, from the

differences between experimental and theoretical values conclusions may be drawn about the interaction potential used in the calculations.

With respect to the purity of the cross sections presented for the $\frac{3}{2}^-$ state it turns out that the calculated contribution of the $\frac{5}{2}^+$ state is for most of the transitions of the order of 4%. For some transitions this contribution is much larger, but it does not prevent us from seeing the symmetry propensity rules as described above.

C. Interaction potential

The potential governing the interaction between an open shell Π -state diatomic molecule and a closed shell atom can be thought as being composed of two potential energy surfaces $V_{A'}$ and $V_{A''}$, having reflection symmetry A' and A'' , respectively, in a plane containing the diatomic and the interacting partner. Alexander¹⁶ showed that for a pure Hund's case (a) molecule the sum potential, $V_{A'} + V_{A''}$, governs the collisional excitation within each spin-orbit multiplet ($F_1 \leftrightarrow F_1, F_2 \leftrightarrow F_2$), whereas the difference potential, $V_{A'} - V_{A''}$, controls the multiplet changing ($F_1 \leftrightarrow F_2$) transitions. Due to symmetry considerations the sum and difference potentials can be expanded as⁴

$$V_{A'} + V_{A''} = \sum_l V_{\Omega}(R) \cdot P_l(\cos \theta) \quad (7)$$

and

$$V_{A'} - V_{A''} = \sum_l V_{\Omega}(R) \cdot P_l^{(2)}(\cos \theta) \quad (8)$$

with $P_l(\cos \theta)$ and $P_l^{(2)}(\cos \theta)$ the regular and associated Legendre polynomials and $V_{\Omega}(R)$ and $V_{\Omega}(R)$ the expan-

sion coefficients for the sum and difference potentials, respectively. For the lowest J -values the OH molecule can be considered as a Hund's case (a) molecule. In case of scattering by Ar the cross sections for spin-orbit multiplet conserving transitions are stronger than those for multiplet changing transitions, when compared to the OH-He results. This may be the result of a larger ratio V_D/V_0 for the OH-Ar potential, where this ratio represents a measure of the efficiency of multiplet changing transitions. From Figs. 6 and 7 it is evident that scattering by Ar is more effective in inducing the Λ -doublet transition ${}^2\Pi_{3/2}, \frac{3}{2}^+ \rightarrow {}^2\Pi_{3/2}, \frac{3}{2}^-$ in the OH radical, than scattering by He. The term in the potential which is directly responsible for this Λ -doublet transition, is the V_{10} term. So a possible explanation for the difference between the Ar and He induced Λ -doublet transitions could be a stronger V_{10} term relative to the higher order odd l potential terms for scattering by Ar than in the case of the OH-He interaction. Furthermore, the spin-orbit conserving transitions are preferred over spin-orbit changing collisional excitations, indicating that the sum potential, $V_{A'} + V_{A''}$, plays a more important role in OH-Ar scattering than the difference potential $V_{A'} - V_{A''}$. However, the differences between Ar and He scattering may result also from different relative velocities for the OH-Ar and OH-He systems, as pointed out in Ref. 6.

Crosley *et al.*⁵ studied the rotational energy transfer in the $v=2$ vibrationally excited state of the electronic ground state of OH scattered by He. Their experiment was performed in bulk circumstances and consequently they obtained rate coefficients instead of cross sections. They found a pronounced parity propensity effect; conservation of total parity is favored in collisions which change the spin-orbit multiplet state. This observation is in agreement with our results for OH ($F_2, v=0$)-He scattering; a clear propensity for parity conserving transitions to the $F_2, J = \frac{1}{2}$ state is observed both for transitions from the upper $J^P = \frac{3}{2}^+$ state (see Fig. 6) and for transitions from the lower $J^P = \frac{3}{2}^-$ state (see Fig. 8). For excitation to the $F_2, J = \frac{3}{2}$ state this parity propensity is less clear. The cross section in Fig. 6 for excitation to the $F_2, J^P = \frac{3}{2}^-$ state in fact represents the sum cross section for scattering into the $F_2, J^P = \frac{3}{2}^-$ and $\frac{3}{2}^+$ state. The actual value for $\sigma(i \rightarrow F_2, \frac{3}{2}^-)$ will be smaller than the number indicated in the figure and consequently the parity propensity for excitation to the $F_2, J = \frac{3}{2}$ state is also in agreement with the observations of Crosley *et al.*

A strong oscillatory behavior of cross sections was reported by Joswig *et al.*¹⁷ for scattering of NO($X^2\Pi_{1/2}$) by rare gas atoms He, Ne, and Ar. Their experiment yielded relative cross sections $\Sigma_p \sigma({}^2\Pi_{1/2}, {}^1P \rightarrow {}^2\Pi_{\Omega}, J^{P'})$ averaged over both initial $J = \frac{1}{2}$ parity substates. For the multiplet conserving transitions they observed that transitions with $\Delta J = 2n$ are preferred over transitions with $\Delta J = 2n - 1$. In the case of NO-Ar scattering these oscillations are well understood¹⁸ and arise from a dominant V_{20} term in the expansion of the sum potential $V_{A'} + V_{A''}$. A similar oscillatory behavior is observed for ($F_1 \rightarrow F_1$) scattering of OH in the upper $J = \frac{3}{2}$ Λ -doublet state by Ar and He if parity instead of symmetry is considered. Experiment as well as

theory indicate that for $\Delta J = \text{even}$ excitations the parity changing transitions are preferred, whereas for $\Delta J = \text{odd}$ the parity conserving transitions are dominant. The observed propensity to change the symmetry in $F_1 \rightarrow F_1$ transitions indicates that for odd ΔJ the potential terms V_{l0} with l even are dominant relative to the odd l terms, whereas for even ΔJ the reverse situation is present.¹⁸ The strong transition to the $\frac{5}{2}^+$ state can then be explained by a dominant V_{20} term, just as for NO scattering. For OH in the lower $J = \frac{3}{2}$ Λ -doublet state a parity conservation is observed for both $\Delta J = 1$ and 2, which can be explained also by a dominant V_{20} term for these type of transitions.

The difference between the collisional behavior of OH molecules in the upper and lower $J = \frac{3}{2}$ Λ -doublet states originates from the intermediate Hund's case character of OH. The wave functions for these states can be written as the same linear combinations of case (a) basis functions but differing in the symmetry index ϵ . In the matrix-elements of the interaction potential which describe the transition probability to an excited rotational state with a given symmetry ϵ' the contribution of the potential terms V_{l0} and V_{l2} is determined by ϵ and ϵ' and can be completely different for both $J^P = \frac{3}{2}^\pm$ states.

V. CONCLUSIONS

In this paper we report parity resolved relative state-to-state cross sections for rotational excitation of OH ($X^2\Pi$) by collisions with He and Ar. In a crossed molecular beam apparatus the OH radicals are produced by generating an electrical discharge in a molecular pulse, containing an H_2O in Ar gas mixture. Two kinds of initial state preparation are applied. The lowest rotational state $|{}^2\Pi_{3/2}, J = \frac{3}{2}\rangle$ is prepared by rotational cooling of the OH molecules in a supersonic expansion. Further state selection of the $|{}^2\Pi_{3/2}$ state, $J^P = \frac{3}{2}^+\rangle$ is achieved by electrostatic state selection in a hexapole electric field. After state preparation the primary beam is colliding with the target beam, containing the rare gases He or Ar. Checks have been performed in order to be sure that single collision conditions are fulfilled, facilitating the data reduction. The rotational energy transfer in both spin-orbit multiplets of the OH ($X^2\Pi_i$) radical is studied by means of LIF spectroscopy of the $A \leftarrow X$ electronic transition of the molecule. Cross sections have been obtained for both the upper, $J = \frac{3}{2}^+$, and, the lower, $J = \frac{3}{2}^-$, Λ doublet states.

Scattering by Ar causes preferentially $\Delta J = 0$ (Λ -doublet) and $\Delta J = 1$ spin-orbit conserving transitions. The spin-orbit changing collisions are weaker by an order of magnitude which indicates that the sum potential $V_{A'} + V_{A''}$ is larger than the difference potential $V_{A'} - V_{A''}$. For OH-He collisions the cross sections for spin-orbit conserving rotational excitation are in the same order of magnitude as those for multiplet changing transitions. Remarkable is the weakness of the Λ -doublet transition induced by He scattering. A clear difference is observed for scattering of OH in the lower and in the upper $J = \frac{3}{2}$ Λ doublet state. For the upper state, $\frac{3}{2}^+$, a clear propensity for symmetry

changing $F_1 \rightarrow F_1$ transitions is observed for both Ar and He collisions. For scattering out of the lower state, $\frac{3}{2}^-$, no propensity for the symmetry is observed; in the transitions to the $\frac{5}{2}^\pm$ and $\frac{7}{2}^\pm$ states there is a preference for parity conservation.

The obtained cross sections are compared with theoretical values from quantum scattering calculations and show, for most cases, remarkably good agreement. Deviations are observed for scattering of OH in the $\frac{3}{2}^-$ state. In case of He collisions the strongest $F_1 \rightarrow F_1$ transition observed is to the $\frac{5}{2}^-$ state which should be much weaker according to the theory. In scattering by Ar the obtained cross sections for $F_1 \rightarrow F_2$ transitions show poor agreement with calculated values.

The present experiment shows that it is possible to study state-to-state collision dynamics even for molecules having no isolated, single rotational ground state. An important conclusion to be drawn is that even for an initial state distribution which seems quite pure at first sight sizeable effects can still be produced by weakly populated states. These states may have large cross sections for transitions to specific states which are only weakly coupled to the "initial" state. This is illustrated by the spin-orbit changing collisions where parity propensity rules which are predicted by theory could not be observed due to scattering out of the 6% populated $J=\frac{5}{2}$ state.

As mentioned earlier the state-to-state cross sections for OH-H₂ scattering have important astrophysical relevance. In a forthcoming paper we discuss a similar collision experiment as the one described in this article, but with collision partners *para*-H₂ and normal-H₂.

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- ¹P. Andresen, N. Aristov, V. Beushausen, D. Häusler, and H. W. Lülf, *J. Chem. Phys.* **95**, 5763 (1991).
- ²R. G. MacDonald and K. Liu, *J. Chem. Phys.* **91**, 821 (1989).
- ³M. H. Alexander, *Chem. Phys.* **92**, 337 (1985).
- ⁴P. J. Dagdigian, M. H. Alexander, and K. Liu, *J. Chem. Phys.* **91**, 839 (1989).
- ⁵G. A. Raiche, J. B. Jeffries, K. J. Rensberger, and D. R. Crosley, *J. Chem. Phys.* **92**, 7258 (1990); I. J. Wyson, J. B. Jeffries, and D. R. Crosley, *ibid.* **94**, 7547 (1991).
- ⁶H.-J. Werner *et al.* *J. Chem. Phys.* (submitted).
- ⁷C. Chakravarty, D. C. Clary, A. Degli-Esposti, and H.-J. Werner, *J. Chem. Phys.* **93**, 3367 (1990).
- ⁸A. Vegiri and S. Farantos, *J. Phys. Chem.* **92**, 2723 (1988); S. Farantos and A. Vegiri, *ibid.* **92**, 2719 (1988).
- ⁹A. Jörg, A. Degli-Esposti, and H.-J. Werner, *J. Chem. Phys.* **93**, 8757 (1990).
- ¹⁰A. Jörg, U. Meier, and K. Kohse-Höinghaus, *J. Chem. Phys.* **93**, 6453 (1990).
- ¹¹A. Degli-Esposti and H.-J. Werner, *J. Chem. Phys.* **93**, 3351 (1990).
- ¹²M. Drabbels, Ph.D. thesis, University of Nijmegen.
- ¹³J. Schleipen and J. J. ter Meulen, *Chem. Phys.* **156**, 479 (1991).
- ¹⁴J. Schleipen, J. J. ter Meulen, and A. Offer, *Chem. Phys.* **171**, 347 (1993); J. Schleipen, J. J. ter Meulen, G. C. M. van der Sanden, P. E. S. Wormer, and A. van der Avoird, *Chem. Phys.* **163**, 161 (1992); G. C. M. van der Sanden, P. E. S. Wormer, A. van der Avoird, J. Schleipen, and J. J. ter Meulen, *J. Chem. Phys.* **97**, 6460 (1992).
- ¹⁵P. J. Dagdigian, in *Atomic and Molecular Beam Methods*, edited by G. Scoles (Oxford University, Oxford, 1988), Vol. 1.
- ¹⁶M. H. Alexander, *J. Chem. Phys.* **76**, 5974 (1982).
- ¹⁷H. Joswig, P. Andresen, and R. Schinke, *J. Chem. Phys.* **85**, 1904 (1986).
- ¹⁸T. Orlikowski and M. H. Alexander, *J. Chem. Phys.* **79**, 6006 (1983).