INELASTIC COLLISIONS OF INTERSTELLAR MOLECULES

Experiment versus Theory

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Abstract. The rotational energy transfer of NH_3, OH and D_2CO in inelastic collisions with He and H_2 is studied in a crossed molecular beam experiment. The molecules are prepared in a single initial state by rotational cooling in an adiabatic expansion followed by electrostatic state selection. Relative state-to-state cross sections are determined by measuring the collision induced redistribution of the population of the initial state by using state selective laser detection techniques. The results for NH_3 and OH are compared to theoretical values obtained from quantum calculations. Except for NH_3 – He where theory predicts a parity selection rule for transitions to the 3_3 and 4_3 states, which is not observed in the experiment, good agreement between experiment and theory is obtained.

1. Introduction

Inelastic collisions with H_2 or He form a dominant process in the rotational energy transfer of interstellar molecules. Knowledge of the state-to-state collision cross sections is needed to explain the observed anomalous non-thermal or maser radiation. In most models either theoretical values for these cross sections are used or experimental data on averaged collision rates since state-to-state cross sections are usually not available. The rates obtained from line broadening or pump-probe experiments involve, however, a manifold of inelastic transitions from or to the probed energy state. The determination of a specific state-to-state cross section requires conditions which are not easily met in a conventional gas cell experiment. First the initial state must be earmarked, secondly not more than one single collision should take place, and thirdly the collision induced redistribution of population has to be probed by a state selective detection technique. The
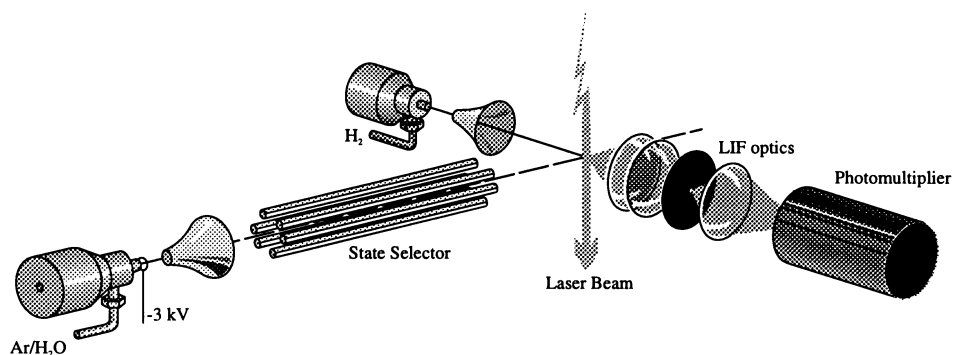
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Figure 1. Artists impression of the crossed molecular beam experiment. The setup shown is for OH, but is basically the same for NH_3 and D_2CO.

last requirement is easiest to fulfill by the use of sensitive laser detection techniques, such as LIF (laser-induced-fluorescence) or REMPI (resonance-enhanced multi-photon ionization) detection. With respect to the other two conditions, the preparation of a single initial state and the occurrence of only a single collision event, these can in principle be met in a crossed molecular beam experiment. The density of the He or H_2 (secondary) beam is then adjusted such that the molecules of the other (primary) beam typically undergo on the average 0.2 to 0.3 collisions. The preparation of the initial state is achieved by rotational cooling in the adiabatic expansion of the primary beam. A first crossed molecular beam experiment on OH radicals was reported by Andresen et al. (1991) in which the rotational energy transfer from the $J = 3/2$ ground state was studied. Since both Λ-doublet states were prepared the results are relative cross sections averaged over the two doublet states. Recently we reported a crossed beam experiment on OH – Ar collisions in which the molecules in the lower $J = 3/2$ doublet state (of *e*-symmetry) are deflected out of the beam by an electrostatic state selector (Schreel et al., 1993; Schreel et al., 1996). As a result Λ-doublet state resolved cross sections are obtained for transitions from the upper Λ-doublet state (of *f*-symmetry). Similar experiments were performed before on NH_3 (Schleipen & Ter Meulen, 1991; Schleipen et al., 1992; Schleipen et al., 1993) and H_2CO (Van Hulst et al., 1987a; Van Hulst et al., 1987b). In these experiments the electrostatic state selection was applied for para-NH_3, where the ground rotational state is the $J_K = 1_1$ inversion doublet, as well as for ortho-H_2CO, with the $J_K = 1_1$ K-doublet as the lowest state.

In this overview the results for the inelastic scattering of OH, NH_3 and D_2CO by He and H_2 are summarized. The formaldehyde isotope D_2CO

was chosen instead of H_2CO because of a higher LIF detection efficiency by an order of magnitude. For OH and NH_3 the measured cross sections are compared to theoretical values obtained from quantum calculations, which are mostly based on *ab-initio* intermolecular potentials. In case of OH also collisions with para-H_2 will be considered.

2. Experiment

A schematic overview of the experimental set up is shown in Fig. 1. The crossed molecular beam machine is described in full detail elsewhere (Schreel et al., 1993; Schleipen & Ter Meulen, 1991; Van Hulst et al., 1987b). Two molecular beams are crossed perpendicularly in a high vacuum chamber, using pulsed valves, except for the measurements on formaldehyde where both beams are continuous. The primary beam contains the NH_3, OH, or D_2CO molecules seeded in Ar. The OH molecules are produced in an electrical discharge in an H_2O/Ar mixture at the exit hole of the pulsed valve. In the adiabatic expansion the molecules are cooled down to the rotational ground state, which except for ortho-NH_3 is a doublet. In order to prepare only a single initial state the molecules in the lower doublet state are deflected from the beam axis. As a result a nearly pure single state distribution is obtained; in all measurements the fraction of molecules in the prepared initial state was between 90 and 95%.

The rotational state distribution of OH and D_2CO is probed by LIF at 308 nm and 325 nm, respectively, whereas NH_3 is detected by (2+1) REMPI via the $\tilde{B}, v' = 0$ and 1 states at 337 nm and 332 nm, respectively. In case of OH and NH_3 a pulsed laser beam is focused in the collision center and the produced photons (LIF) or ions (REMPI) are detected by a photomultiplier or a particle multiplier tube, respectively. The D_2CO molecules are detected by a cw laser beam at 325 nm at a distance of 83 mm from the collision center. By rotating the probe area around the collision center differential cross sections are measured.

In all cases the observed signal is linearly proportional to the population of the probed state, which enables the direct determination of relative state-to-state cross sections. Elaborate checks upon the single collision condition have been performed. It can be shown that in case of multiple collisions the scattering signal is no longer linearly proportional to the secondary beam density (Schleipen & Ter Meulen, 1991). All measurements were therefore performed at He and H_2 densities far below the onset of a non-linear behaviour of the scattering signal.
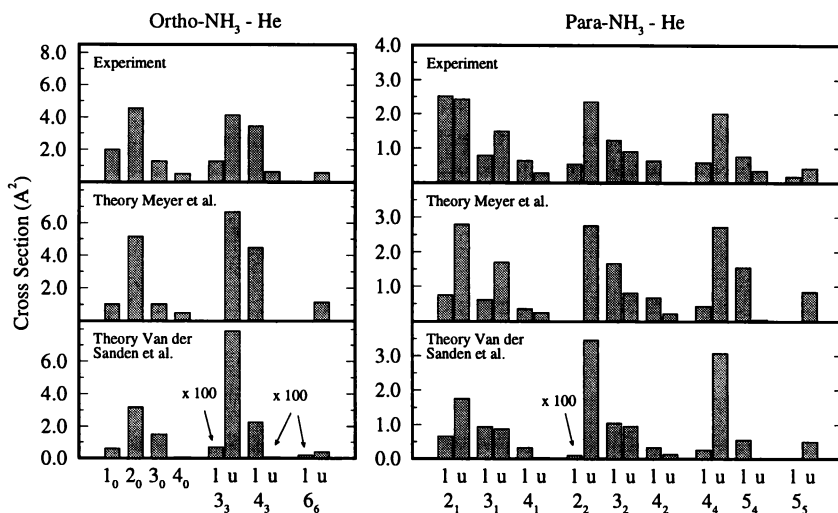
Figure 2. State-to-state cross sections for rotational energy transfer of ortho-$NH_3(0_0)$ and para-$NH_3(1_1 u)$ in collisions with He. The experimental results are compared to theoretical values from Meyer et al. (1986) and van der Sanden et al. (1995).

3. Experimental results and comparison with theory

3.1. NH_3

The cross sections for He- or H_2-scattering of NH_3 were measured for transitions with $|\Delta K| = 0, 3$ and 6 and with ΔJ up to 6. The collision energy is 435 cm^{-1} for NH_3 – He and 596 cm^{-1} for NH_3 – H_2. From the measurements relative cross sections are obtained with an accuracy of 10%. Absolute values are derived by scaling the experimental results to theoretical values in such a way that the sum of the cross sections for ortho-NH_3, as well as for para-NH_3, is the same for experiment and theory. The absolute data are listed in (Schleipen & Ter Meulen, 1991).

3.1.1. NH_3 – He

The experimental results for collisions with He are presented graphically in Fig. 2. The bars in Fig. 2 give the magnitude of the measured cross sections. For each excited J_K state two bars are plotted for the two parity states, except for $K = 0$. Also plotted in Fig. 2 are theoretical values calculated by Meyer et al. (1986) and Van der Sanden et al. (1995). Meyer et al. performed a Coupled States (CS) calculation at a collision energy of 789 cm^{-1} using an experimentally modelled intermolecular potential. Van der Sanden et al. did calculations at the experimental collision energy applying the more accurate quantum mechanical Close Coupling (CC) method

using an *ab-initio* potential. As can be seen from the figure, apart from parity propensities, there is a reasonably good qualitative agreement between both calculations and the experimental results. For ortho-NH_3 the cross section $\sigma(0_0 \to 2_0)$ is considerably larger than $\sigma(0_0 \to 1_0)$, as theory predicts. The experimental ratio of these cross sections of 2.3 is, however, noticeably smaller than the calculated ratio of 5.2. The transitions to the 3_3 and 4_3 states are relatively strong; when summing the cross sections for the transitions to the two parity states the experimental results are very close to the values calculated by Meyer et al. The calculations by Van der Sanden et al. seem to overestimate the sum of the cross sections for the transitions to the 3_3 doublet and to underestimate the transitions to the 4_3 doublet. Also with respect to the cross sections for para-NH_3 the experimental parity summed values show a better agreement with the calculated values of Meyer et al. than with the results of Van der Sanden et al.

Strong deviations show up when considering the excitation of the two parity states belonging to a specific J_K state. Whereas theory predicts strong parity propensity rules, particularly for transitions to the 3_3 and 4_3 states for ortho-NH_3 and to the 2_2 state for para-NH_3, this is not observed in the experiment. For a similar situation observed for NH_3 – Ar (Schleipen et al., 1992) it was shown by Van der Sanden et al. (1992) that the complete absence of cross sections for transitions to the lower 3_3 and the upper 4_3 doublet state is an artifact of the CS approximation due to the neglect of Coriolis terms in the Hamiltonian. When applying the CC approximation, where these terms are taken into account, significant transition probabilities were obtained. However, when applying the CC approximation to the NH_3 – He system they found that these Coriolis terms have little influence resulting in still very small but non-zero cross sections, as can be seen in Fig. 2. The same authors also showed that the fact that the initial state preparation in the experiment is not perfect may cause non-negligible effects. States which are weakly populated, *i.e.* the 1_0 state for ortho-NH_3 and the lower 1_1 state for para-NH_3, may provide a significant contribution to otherwise small cross sections. Taking this into account the authors found a population transfer up to even 40% of the observed values for $\sigma(0_0 \to 3_3 l)$ and $\sigma(0_0 \to 4_3 u)$, which, however, still leaves a non-understood discrepancy between theory and experiment.

3.1.2. NH_3 – H_2

In Fig. 3 the measured cross sections for transitions induced by collisions with H_2 are presented. In the same figure also theoretical values of Ebel et al. (1990) and of Offer & Flower (1990) are shown. The experimental values are scaled to the calculated values of Ebel et al. Strong differences with the NH_3 – He system can be noticed. For ortho-NH_3 the transition
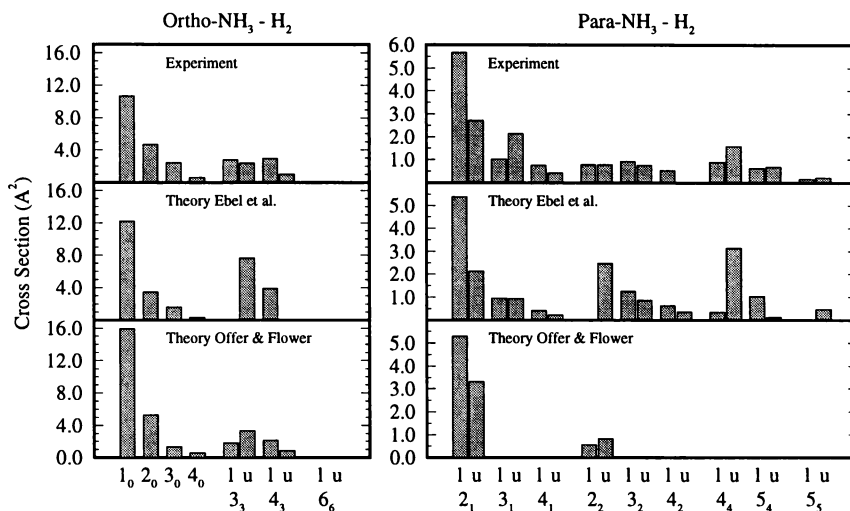
Figure 3. State-to-state cross sections for rotational energy transfer of ortho-$NH_3(0_0)$ and para-$NH_3(1_1u)$ in collisions with H_2. The experimental results are compared to theoretical values from Ebel et al. (1990) and Offer & Flower (1990).

to the 1_0 state is now the strongest one, as predicted also by theory. For para-NH_3 there is a strong preference for the excitation to the lower 2_1 state, in agreement with theory. The parity propensities as observed in He collisions do not show up so strongly. When summing the cross sections for the transitions to the two parity states belonging to the same J_K state a reasonably good agreement between experiment and theory is obtained. The calculations by Ebel et al. were performed in the CS approximation at a collision energy of 604 cm^{-1}. As for He the cross sections for the transitions to the lower 3_3 and upper 4_3 states are per definition zero in this CS framework, whereas the transition to the lower 2_2 state is extremely weak. Offer & Flower performed CC calculations and expanded the potential in a more accurate way than Ebel et al. As a result they obtained relatively large cross sections for the transitions to the 3_3l, 4_3u and 2_2l states. Some deviations between experiment and theory are still present, which might be due to the presence of H_2 ($J = 2$) in the secondary beam, which is not taken into account in the comparison with theory (see the OH – H_2 results below).

3.2. OH

The measurements on OH – He and OH – H_2 collisions have been performed both in the presence and in the absence of the electrostatic state selector. In the first situation the initial state is the upper (f) $\Pi_{3/2}, J = 3/2$, Λ-
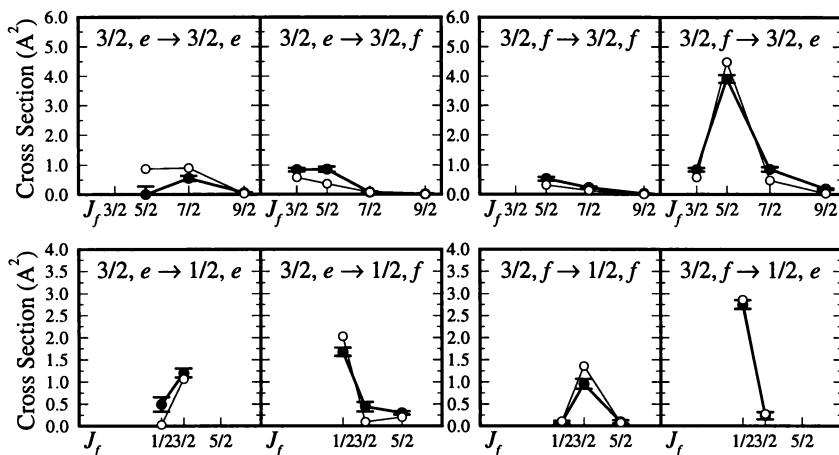
Figure 4.   State-to-state cross sections for rotational energy transfer of OH $(\Pi_{3/2}, J = 3/2)$ in the upper (f) and lower (e) Λ-doublet state in collisions with He. The experimental results ($\bullet$) are compared with theoretical ($\circ$) values from Esposti et al. (1995).

doublet state, in the latter case both the upper and the lower (e) state are populated. By "subtracting" the results for the upper state the cross sections for transitions from the lower Λ-doublet state are obtained (Schreel et al., 1996). In addition to transitions within the $\Pi_{3/2}$ rotational ladder up to $J = 9/2$ also spin-orbit changing transitions to the $\Pi_{1/2}$ ladder up to $J = 5/2$ are studied. The collision energy is 394 cm^{-1} for He scattering and 595 cm^{-1} for H$_2$ scattering. Details of the measurements and numerical values for the obtained cross sections are given in (Schreel et al., 1993) for OH – He and in (Schreel et al., 1996) for OH – H$_2$.

3.2.1. *OH-He*

The measured cross sections are presented in Fig. 4. In the left hand side the results for transitions from the lower $J = 3/2, \Lambda$-doublet state are shown, in the right hand side the results for the upper Λ-doublet state as the initial state are given. The upper part concerns the transitions within the $\Pi_{3/2}$ ladder, whereas the spin-orbit changing transitions are considered in the lower part. In addition, symmetry changing $(e \leftrightarrow f)$ and symmetry conserving $(e \leftrightarrow e, f \leftrightarrow f)$ transitions are distinguished. It should be noted that the lower Λ-doublet states studied are all of e-symmetry and the upper ones of f-symmetry. In the figure also theoretical values from Esposti et al. (1995) obtained in a CC calculation using an *ab-initio* potential are given. The experimental values are scaled to the calculated ones in such a way that the sum of all cross sections given in Fig. 4 is set equal to the
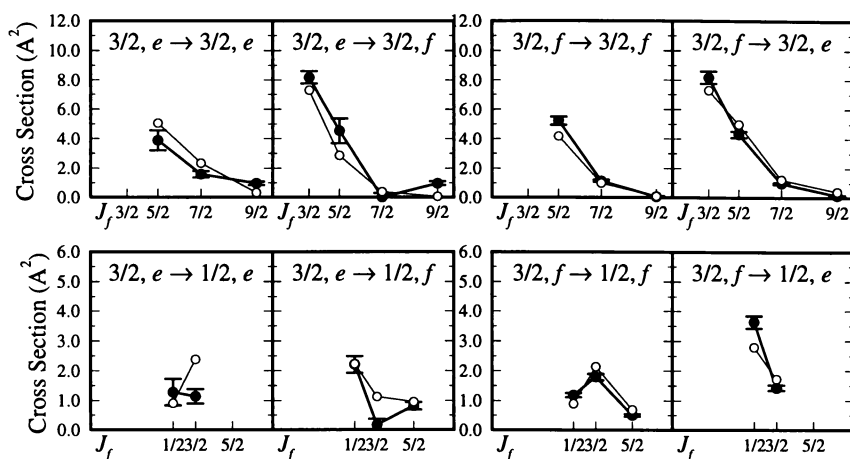
Figure 5.   State-to-state cross sections for rotational energy transfer of OH ($\Pi_{3/2}$, $J = 3/2$) in the upper (f) and lower (e) Λ-doublet state in collisions with n-H_2. The experimental results ($\bullet$) are compared with theoretical values ($\circ$) from Offer et al. (1994).

sum of the theoretical results. Most striking is the relatively large cross section for the transition $3/2, f \rightarrow 5/2, e$, in contrast to the much weaker $3/2, e \rightarrow 5/2, f$ transition. Unexpected was also the relatively weak Λ-doublet transition. These features are in accordance with the theoretical predictions. Also the other experimental results are in good agreement with theory, apart from the transition $3/2, e \rightarrow 5/2, e$, which is observed to be much weaker than calculated. The differences between the cross sections for transitions from the upper and the lower doublet state have not been observed before and are caused by interferences of the matrix elements of the intermolecular potential due to the intermediate Hund's case character of OH.

3.2.2.   *OH – H_2*

Measurements are performed for both n(ormal)-H_2, with an ortho : para ratio of 3 : 1, and p(ara)-H_2. The results for n-H_2 are presented in Fig. 5. Strong differences with He scattering can be seen. First, contrary to He scattering the Λ-doublet transition is now preferred above all other transitions. Secondly, transitions to the 5/2 state do not show any symmetry dependence; the same holds for transitions to the 7/2 state except for $3/2, e \rightarrow 7/2, f$ with a nearly zero cross section. The cross sections for scattering by p-H_2 are presented in Fig. 6. The p-H_2 beam consists of H_2 molecules in both $J = 0$ and $J = 2$ in a ratio of 2 : 1. Compared to n-H_2 the Λ-doublet cross section is considerably smaller and clear symmetry dependences show up with respect to transitions to the 5/2 state. It turns
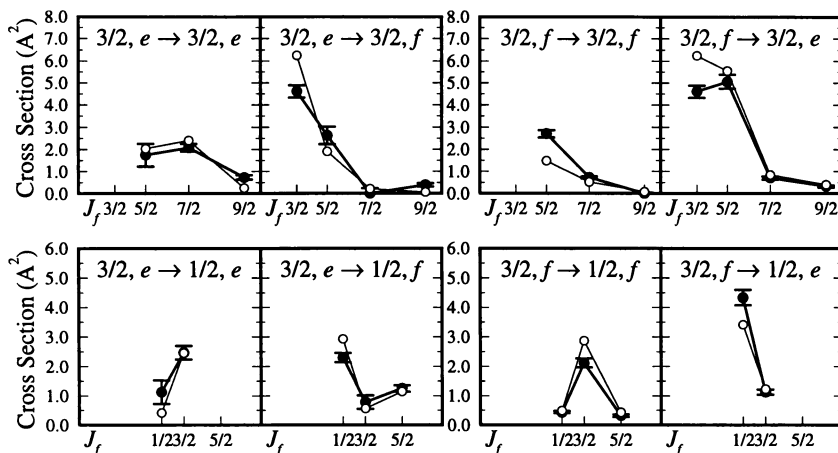
Figure 6. State-to-state cross sections for rotational energy transfer of OH $(\Pi_{3/2}, J = 3/2)$ in the upper (f) and lower (e) Λ-doublet state in collisions with p-H$_2$. The experimental results ($\bullet$) are compared with theoretical values ($\circ$) from Offer et al. (1994).

out that the J- and parity dependence of the cross sections is in between that for n-H$_2$ and He. In order to find out what the influence is of the $J = 2$ state, measurements were performed with a p-H$_2$ beam consisting of a $(J = 0) : (J = 2)$ ratio of $1 : 1$. In this case the Λ-doublet cross section increased by a factor of 4, from which we conclude that the value given in Fig. 6 is determined by collisions with H$_2(J = 2)$. In other words a relatively small cross section for the Λ-doublet transition is expected in case of H$_2(J = 0)$ scattering, similar to He. Another strong indication that H$_2(J = 0)$ behaves like He is given by the ratio of the cross sections $\sigma(3/2, f \rightarrow 5/2, e)/\sigma(3/2, f \rightarrow 5/2, f)$, which strongly increases when the fraction of H$_2(J = 0)$ in the beam increases. In case of He this ratio is 7.3. A comparison to the results of quantum calculations by Offer et al. (1994) based on an *ab-initio* potential shows a surprisingly good correspondence between theory and experiment. Some deviations are still present, particularly for p-H$_2$, which probably is due to a lower accuracy of the calculations involving H$_2$ $(J = 2)$.

3.3. D$_2$CO – H$_2$

For D$_2$CO differential cross sections were measured at a collision energy of 134 cm^{-1} for transitions from the upper 1_1 doublet state, 1_{10}, to the lower doublet state, 1_{11}, and to the upper and lower 2_1 states, 2_{11} and 2_{12}, respectively. The results are plotted in Fig. 7 as a function of the angle with the beam axis. Also included is the elastic cross section for the
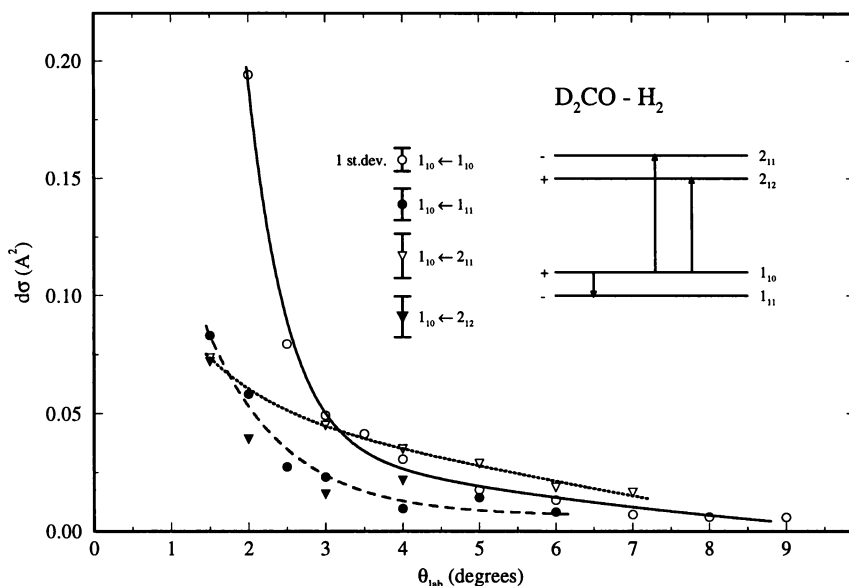
Figure 7.   Absolute state-to-state differential cross sections for $D_2CO(1_{10})$ in collisions with H_2.

1_{10} state showing a rapid decrease for larger angles. The inelastic cross sections are an order of magnitude smaller at small angles. The total state-to-state cross section is derived by integrating the differential cross section over the full angular range of the scattering. Hereto the sensitivity was, unfortunately, not high enough. However, as can be seen from the figure the differential cross section for the $1_{10} \rightarrow 2_{11}$ transition is systematically larger than the cross sections for the $1_{10} \rightarrow 2_{12}$ and $1_{10} \rightarrow 1_{11}$ transition, which leads to the conclusion that the total cross section $\sigma(1_{10} \rightarrow 2_{11})$ is larger than the total cross sections $\sigma(1_{10} \rightarrow 2_{12})$ and $\sigma(1_{10} \rightarrow 1_{11})$. No calculations on the $D_2CO - H_2$ system have been reported in literature thus far. Green (1979) has calculated cross sections for $H_2CO - H_2$ at a collision energy of 200 cm^{-1}, and obtained cross sections which indeed are larger for the rotational transition $1_1 \rightarrow 2_1$ than for the K-doublet transition by a factor of 1.6. However, the calculated cross sections $\sigma(1_{10} \rightarrow 2_{11})$ and $\sigma(1_{10} \rightarrow 2_{12})$ were found to be equal, which deviates from the experiment. Since the rotational spacings of H_2CO and D_2CO in the $K_{-1} = 1$ ladder differ by not more than 20%, this discrepancy can most likely be ascribed to the fact that only H_2 $(J = 0)$ is considered in the calculations.

4. Conclusions

Parity resolved state-to-state cross sections are obtained for the rotational energy transfer of OH, NH$_3$ and D$_2$CO in collisions with He and H$_2$. For OH and NH$_3$ the results are in good agreement with theory. Some discrepancies are still present, particularly with respect to the predicted parity propensities in NH$_3$ – He, which are not observed in the experiment. The overall good agreement between theory and experiment justifies an extrapolation of the calculations to the lower collision energies in the interstellar space.

Acknowledgements

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Discussion

Herbst: What is the collision energy?

Ter Meulen: The collision energy for both the NH_3 and the OH scattering is about 600 cm^{-1}. It is not easy to do these experiments at collision energies which are similar to those in interstellar sources. In order to obtain cross sections at those low energies one should extrapolate the data by making use of quantum calculations. The good agreement between the present experimental results and theory shows that nowadays these calculations can be performed up to a high degree of reliability.

Kurtadikar: Has the experiment the facility to vary the temperature during collisions? How is it done and what is the range of temperature variation that can be achieved? What are the pressure limitations?

Ter Meulen: It is possible to vary the temperature by choosing different seeding gases, like Xe or Ne, as we did for $H_2CO - H_2$. In combination with H_2 cooling we could vary the temperature between 100 and 900 K. Lower temperatures can be obtained by reducing the angle between the two beams, which, however, requires a complicated reconstruction of the molecular beam machine. The pressure in the collision area is very low ($\sim 1.10^{-6}$ mbar) and does not influence the temperature.

Wilson: In astrophysical situations one of every five collision partners are Helium atoms.

Ter Meulen: Since collisions of NH_3 with H_2 do not create a population inversion between the 3_3 states — at least not at our collision energy — one should consider collisions with He atoms as a possible pumping mechanism. Although there is still a disagreement between experiment and theory about the excitation to the lower 3_3 doublet state, it is clear that there is a strong preference for transitions to the upper 3_3 state. So for He a population inversion can be expected.

Irvine: As was pointed out this morning for cometary studies we need cross sections with H_2O. What are the prospects for obtaining these?

Ter Meulen: $H_2O - H_2$ might be the next system which we will study. There is a big need for these cross sections, and ab-initio potentials seem to be available now.