THE HYDROGEN MOLECULE AS A COLLISION PARTNER

Takeshi Oka
Herzberg Institute of Astrophysics
National Research Council of Canada
Ottawa, Ontario, Canada

Because of its abundance in molecular clouds, the hydrogen molecule is the most important collision partner in a discussion of thermal equilibrium or non-equilibrium in most interstellar molecules. The purpose of this talk is to summarize the properties of the $\text{H}_2$ molecule as a collision partner based on laboratory experiments on $\text{NH}_3$-$\text{H}_2$ collisions.

The basic process to be studied is shown in Figure 1. The $\text{NH}_3$ molecule interacts with the $\text{H}_2$ molecule and changes its inversion-rotation state $(J', K', P' + J, K, P)$, where the quantum numbers $J, K, P$ correspond to the total angular momentum, its projection along the molecular axis, and the parity, respectively.

![Diagram of the elementary process](image)

Fig. 1. The elementary process
Note that the interaction does not change the rotational quantum number $j$ of the $H_2$ molecule because of the large energy separation between the levels. (The smallest separation in one spin species is $\sim 360 \text{ cm}^{-1} \sim 520 \text{ K}$ between the $j=2$ and $j=0$ levels, which is much larger than either the energy change in NH$_3$ or $kT$, not only in interstellar space but also in the laboratory. The transition between the $j=1$ and $j=0$ levels is forbidden because of the ortho-para rule). The $\Delta j \neq 0$ transitions of $H_2$ are neglected in the following discussion because of their small probability.

1. **THE INNER CORE-OUTER SHELL MODEL OF H$_2$**

   The potential energy between a polar molecule and a hydrogen molecule can be divided into two parts:

   (a) The long range dipole-quadrupole potential,

   $$V(r) = -\frac{1}{r^2} \left[ e \cdot Q \cdot \mu - \frac{5}{2} (e \cdot Q \cdot e)(e \cdot \mu) \right]$$

   where $\mu$ is the dipole moment of the polar molecule, $Q$ is the quadrupole tensor of the $H_2$ molecule and $e = r/r^3$ is the unit position vector between the two molecules. The higher multipole moments are neglected.

   (b) The shorter range potential due to induction, dispersion and valence forces whose radial part is approximated for example by the Lennard-Jones potential. The angular dependent part of such a potential causes rotational transitions in NH$_3$.

   The former potential plays the major role for weaker collisions with large impact parameters, the latter for stronger collisions with small impact parameters. Thus we can consider a model in which the $H_2$ molecule as a collision partner consists of two parts, a hard core and a soft outer shell. Note that the He atom, which is the next important collision partner, has only the hard core.

2. **FOUR-LEVEL DOUBLE RESONANCES**

   The existence of the double structure is most clearly revealed by four-level double resonance experiments (Oka 1973). In these experiments two microwave radiation fields $\nu_p$ and $\nu_s$ and a low pressure ($\sim 1$ torr) mixture of NH$_3$ and H$_2$ (or for comparison He) with a mixing ratio of $\sim 1:100$ are used. The first radiation $\nu_p$ (pump radiation with a power of $\sim 1$ W) saturates an inversion transition and thus introduces a non-Boltzmann population in the rotational
levels \((J, K)\). This population anomaly is then transferred to other levels by collisions. The second radiation vs (signal radiation with a power of \(\sim 1 \mu W\)) monitors the result of the population transfer by detecting a variation in intensity of other inversion lines \((J', K')\). Using many combinations of \((J, K)\) and \((J', K')\) we can study systematically the collisional process shown in Figure 1.

The effect of the outer shell is most clearly seen when we choose \((J' = J-1, K' = K)\) levels which are connected to the pump levels by the dipole selection rules (Figure 2).

\[
\Delta K = 0
\]

Fig. 2 The four-level microwave double resonance experiments, for dipole-allowed transitions. The pump is shown by the bold arrow, the signal by the thin arrow, and the collision-induced transitions by wavy arrows. The \(H_2\) molecule and the He atom act very differently as collision partners.

For the \(NH_3-H_2\) experiment the signal intensity is increased by pumping, indicating that the \(NH_3\) molecule changes its parity by collision. This is expected from the first order treatment of the dipole-quadrupole interaction. On the other hand for the \(NH_3-\text{He}\) experiment the signal intensity is decreased by pumping, indicating that the parity of the \(NH_3\) molecule is preserved in the collision. These experiments demonstrate the qualitative difference between the core and the outer shell as perturbers.

The effect of the inner core of \(H_2\) is seen when we choose a double resonance system with \(K' \neq K\). Such transitions are not dipole-allowed and are caused by stronger collisions. For some reasons which are not completely clear to me, even such stronger collisions have some parity rules and double resonance signals are easily observed. If we compare the relative intensities of such signals for the \(NH_3-H_2\) and the \(NH_3-\text{He}\) mixtures, we observe a remarkable similarity, as shown in Figure 3. This indicates that in spite of the fact that the \(H_2\) molecule
and the He atom have cores of different shapes, they act very similarly for strong collisions.

\[ \Delta K \neq 0 \]

![Graph showing results of four-level microwave double resonance for dipole-forbidden transitions \((\Delta K = \Delta J, J \neq 0)\). Here the \(H_2\) molecule and the He atom act very similarly on \(NH_3\) as the collision partners.]

3. \(H_2\) IN \(J=0\)

In the collision process shown in Figure 1 in which the \(H_2\) molecule does not change its rotational state, the \(H_2\) molecule in the ground rotational level \(J=0\) acts as if it does not have the outer shell. This is expected from the matrix element of the dipole-quadrupole potential \(V(r)\) which can be rewritten (Oka 1973),

\[ V(r) = -\frac{8\sqrt{\pi}}{r^5} \mu Q \sum_{m_1, m_2, m} \left( \begin{array}{c} 1 \\ 2 \\ 3 \end{array} \right) D^3_{0,0,0} (\Omega_r) D^1_{0,1,0} (\Omega_\mu) D^2_{0,0,0} (\Omega_Q) \]

where \(D_{n,m}^{l} (\Omega)\) are rotation matrices for the spatial orientations \(\Omega_r\), \(\Omega_\mu\), and \(\Omega_Q\) of the position vector \(r\), the dipole moment \(\mu\), and the quadrupole moment \(Q\), respectively. It is seen from this formula that \(\langle j|V(r)|j\rangle = 0\) for \(j=0\) because \(\langle 0|D^2_{0,0,0} (\Omega_Q)|0\rangle = 0\), that is, the \(H_2\) molecule in the \(j=0\) level behaves as a collision partner as if it does not possess the quadrupole moment. Thus we arrive at the models shown in Figure 4.

![Models of the He atom and the \(H_2\) molecule as collision partners.]

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4. PRESSURE BROADENING

The special characteristics of the $\text{H}_2$ molecule with $j=0$ can be seen most directly from pressure broadening of spectral lines. There is a large difference in the percentages of the $j=0$ $\text{H}_2$ molecules in normal-$\text{H}_2$ and para-$\text{H}_2$ (18.4% in normal-$\text{H}_2$ and 73.2% in para-$\text{H}_2$ at dry ice temperature; 13.0% and 51.7% at room temperature). This can be used to distinguish the effect of the $j=0$ $\text{H}_2$ molecules from the rest. Figure 5 shows a recent measurement in the infrared region. A difference frequency laser $\text{NH}_3 + \text{H}_2 (154 \text{ Torr, } -66 \text{ C})$

$$\nu, \phi \Omega (3,3)$$

![Graph showing normal and para $\text{H}_2$](image)

Fig. 5. Pressure broadening of the infrared transition line $\nu_1, \phi \Omega (3,3)$ of $\text{NH}_3$, by normal-$\text{H}_2$ and para-$\text{H}_2$ at dry ice temperature. The total pressure is 154 torr for both traces. (D.R. Rao and T. Oka, 1979).

The system was used as a frequency tunable infrared source. The difference between the normal-$\text{H}_2$ and para-$\text{H}_2$ as collision partners is clearly seen. Measurements in the infrared and microwave regions of $\text{NH}_3$ lines showed that the normal-$\text{H}_2$ containing more $j \neq 0$ $\text{H}_2$ is more effective as a perturber than the para-$\text{H}_2$ by a factor of 1.17±0.06 at room temperature and 1.29±0.03 at dry ice temperature. Using the simple assumption that all $j \neq 0$ $\text{H}_2$ molecules have the same collision cross section as partners to $\text{NH}_3$, we determine the ratio of the total collision cross section for the $j \neq 0$ $\text{H}_2$ to that for the $j=0$ $\text{H}_2$ to be

$$\sigma_{j \neq 0} / \sigma_{j=0} = 1.60 .$$

Thus in the model shown in Figure 4, the effect of the outer shell in causing rotation-inversion transitions in $\text{NH}_3$ is 60% of that of the inner core.

It should be noted that although the outer shell is somewhat less effective than the inner core in causing rotation-inversion transitions in $\text{NH}_3$, its effect is concentrated in causing dipole-type transitions and may
dominate for such transitions. The results shown in Figure 2 are understood from such a consideration.

5. ASTROPHYSICAL IMPLICATIONS

From the observations given above, it is seen that any discussion on thermal equilibrium or non-equilibrium of interstellar molecules depends critically on whether the H₂ molecule considered as the collision partner is in the j=0 level or not. In the former case, the H₂ molecule (j=0) acts as the He atom and the results of several theoretical calculations of the (polar molecule-He) system are probably approximately transferrable to the (polar molecule-H₂) system, if allowance is made for a difference between the absolute magnitudes of the cross sections of the two systems (the ratio estimated from pressure broadening is about 1:1.5 for He to H₂ j=0). This type of collision is more likely to cause population anomalies which are required for the maser or the anti-maser action.

On the other hand, the H₂ molecules in j≠0 levels act to reduce such population anomalies. This is because (a) the outer shell of such a H₂ molecule causes efficiently the collision-induced transition between the levels observed by microwave radiation and thus tends to thermalize the population and (b) it also tends to make symmetric the transition rates between various levels of K-type, A-type or inversion doubling. Thus for example the cooling mechanism proposed by Townes and Cheung (1969) for the l₁₁→l₁₁ transition of H₂CO is less likely to work for j≠0 H₂ because (a) the collision-induced l₁₁→l₁₁ transition will reduce the anomaly and (b) the required asymmetry in the rates of the 2₁₁→₁₁₁ and the 2₁₁→₁₁₁ transitions is less likely.

When the H₂ molecules are initially formed on dust grains and released in space, the ortho-para ratio is thought to be statistical, that is, initially there are more ortho-H₂ than para-H₂ (Black and Dalgarno 1976). The ratio of j=0 H₂ to the rest depends on how efficiently the mechanism of H⁺ + o-H₂ → H⁺ + p-H₂ (Dalgarno, Black and Weisheit 1973) thermalizes the two species in the low temperature molecular cloud.

REFERENCES

DISCUSSION FOLLOWING OKA

*Carruthers:* How did you make pure parahydrogen to use in your experiments?

*Oka:* We boil off liquid H₂ then check the pureness of para-H₂ by observing the rotational Raman spectrum.

*Thaddeus:* You can buy pure para-H₂. Presumably it is used by bubble chamber people.

*Oka:* Yes, but the trouble is that suppliers of liquid H₂ for bubble chambers sell only by tons.

*Carruthers:* I think that all of the Copernicus observations of interstellar H₂ are consistent with a thermal ortho to para-hydrogen ratio.

*Oka:* The circumstellar H₂ seems to be all thermalized, but the ratio for dark clouds is not known.

*Townes:* Have you ever been able to make any measurement concerning the refrigeration of formaldehyde?

*Oka:* Yes, Evenson, Freund and I attempted that experiment specifically for the Townes-Cheung four-level system of H₂CO. The result is not conclusive. The main problem is that we cannot simulate the interstellar conditions, especially the temperature.

*W. Watson:* If, in fact, the ortho to para ratio for H₂ is determined by gas-phase exchange processes, and is near the thermodynamic equilibrium value at the temperature of the gas, then in cooler clouds there should be a higher fraction in the para state which causes the H₂CO refrigeration. Do you know of any astronomical studies that would suggest such an effect?

*Oka:* No, I am not aware of any. Whether the ortho-para ratio is indeed thermalized to the low temperature of a cloud depends on the efficiency of the Dalgarno-Black-Weisheit reaction, that is, it depends on the proton density in the cloud. The ortho-para ratio, if thermalized, does not critically depend on temperature as long as the temperature is much lower than 171 K, the excitation level of the j=1 state.

*Omont:* Could you give a value for the ratio of the collisional rates for transitions inside K doublets to the rates of rotational excitation in NH₃?


*Winnewisser:* Do collisions of j=0 H₂ and other H₂ affect differently the K=1 and 2 levels and the K=3 levels of NH₃, i.e. para and ortho ammonia? What would be the difference?

*Oka:* As long as we consider K=0 transitions, there is not much difference between ortho and para NH₃. For K=3 transitions, that is, k = ±1 ↔ ±2 and k = 3 ↔ 0, there is a difference, because the former transition is symmetric for inversion levels while the latter is not.

*T. Wilson:* Are there large differences between the NH₃-H₂ cross-sections for ortho and para-NH₃?

*Oka:* No. If you consider the total cross section there is not much difference. There is no detectable difference in pressure broadening parameters of ortho-NH₃ and para-NH₃, apart from the usual k-dependence.
Toomre: I am a little puzzled. The conversion from ortho to para-NH$_3$ is presumably through the exchange reaction with protons, as is the case with H$_2$, although there may also be some other mechanism. In general it seems that NH$_3$ is approximately in thermal equilibrium, and that would seem to have some bearing on whether H$_2$ is also in thermal equilibrium.

Oka: I am surprised to hear that from you. Your initial measurement of NH$_3$ in Sgr B2 showed much higher intensity in the ortho lines than in the para lines.

Toomre: The ratios are, I would say, not far from the thermal equilibrium values.

Oka: A factor of two?

Toomre: Yes, though our measurement was not very precise.

Oka: Two is a large factor. I think other measurements by Morris et al. and by the Bonn group also show a large difference between ortho and para-NH$_3$. One consideration here is that the conversion between ortho and para-H$_2$ is expected to be slower than that between ortho and para-NH$_3$ or between spin modifications in other polyatomic molecules.

Toomre: Is that true? What is the ammonia colliding with?

Oka: Even if NH$_3$ collides with neutral H$_2$, conversion can occur.

Toomre: Does the collision cause an interchange of hydrogen atoms between the molecules?

Oka: No, there is just a normal collision without chemical reaction.

Toomre: But surely the conversion occurs only by substitution?

Oka: Not necessarily. Ortho-para symmetry in polyatomic molecules is not as rigorous as in H$_2$. There is little mixing of ortho and para species due to nuclear spin-rotation interaction. For example, in spherical top molecules, the different spin modifications can convert easily with each other by collision.

Toomre: I thought that there is a laboratory experiment indicating that collisions with molecular hydrogen cannot vary the NH$_3$ ortho to para ratio, whereas collisions with atomic hydrogen cause very rapid conversion.

Oka: I am not aware of that experiment. As far as I know there has been no observation of transitions between different spin modifications other than for H$_2$ and D$_2$. In other words, nobody has yet produced in the laboratory anomalous spin populations of polyatomic molecules such as formaldehyde, water or NH$_3$.

Toomre: I believe I was told about the experiment by a chemist in Berkeley. I think his reasoning was based on the possibility of reactional substitution. It is not a direct experiment but an experiment associated with deuterium.

Oka: Then I understand.

Thaddeus: I believe that in the liquid phase of hydrogen, it takes about $10^{15}$ collisions to accomplish conversion from ortho to para. Presumably for NH$_3$ the number of collisions is comparable.

Oka: It could be much less.

Thaddeus: But the rate of conversion is still very slow?

Oka: Yes, much slower than normal. My double resonance experiments showed this rather clearly. However, compared with H$_2$ conversion, polyatomic molecules can convert much faster. I might mention that
Professor Curl and his collaborators attempted to make CH₄ molecules with anomalous spin modification ratio. They cooled CH₄ to He temperature, then boiled it suddenly, hoping that, in the same way as H₂, the CH₄ molecules would go to one spin modification at low temperature (there are nuclear magnetic susceptibility measurements indicating this) and boil adiabatically to form anomalous spin species. They could not observe any anomaly. A theoretical calculation shows that such conversion is very fast in CH₄, because the rotational energy levels corresponding to different spin modifications are very close and the mixing due to spin-rotation interaction is large. I spent a few months with Retallack doing the same experiment in NH₃ where theory predicts much slower conversion. We could not detect an anomaly.

Field: I should just like to comment that in experiments involving A¹₂ NH₂ in collisions with H-atoms (and other partners), no ortho-para conversion is observed in rotationally inelastic events.

Oka: That agrees with my own experimental results. However, here we are discussing much slower processes. These slower processes are not likely to be observed in normal laboratory experiments other than those I mentioned earlier.

Dalgarno: I think what is happening in the stellar case is that the interchange of protons will also be effective in the case of NH₃, so NH₃ is thermalized just as H₂ is thermalized. Thus it can be characterized by the same temperature.

Oka: Yes. All I am saying is that there is an extra process which thermalizes NH₃, and therefore NH₃ conversion is at least as fast as H₂ conversion. Now if NH₃ spin modifications are not completely thermalized in interstellar space as observation seems to show, there is more possibility that H₂ spin modifications are not thermalized.

W. Watson: In exchanging the ortho and para forms of NH₃, reactions of the form NH₃ + H₂ → NH₄⁺ + H₂, NH₄⁺ + e → NH₃ + H⁺ may be more important than reactions with H⁺. If so, one would not expect the two forms to be thermalized.

Thaddeus: One point about your laboratory experiments. Even if you cannot go down to the extremely low temperature of interstellar molecules, your results provide a very valuable check of theory, in that theorists should be able to calculate your results just as easily as they can calculate interstellar cross sections.

Oka: I think Sheldon Green has much more difficulty in calculating the high temperature case. At low temperatures his multi-channel equations are much simpler. For the high temperature case he presumably has to worry much more about how to treat the translational motion.

Thaddeus: Then the comparison should be at intermediate temperatures.

Oka: Yes. His calculations come up to liquid-N₂ temperatures and my experiment goes down to dry ice temperature.

Dalgarno: In their present states the theory and observations are mutually orthogonal.