

THE HYDROGEN MOLECULE AS A COLLISION PARTNER

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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 H_2 molecule as a collision partner based on laboratory experiments on NH_3-H_2 collisions.

The basic process to be studied is shown in Figure 1. The NH_3 molecule interacts with the H_2 molecule and changes its inversion-rotation state ($J',K',p' \leftarrow J,K,p$), where the quantum numbers J,K,p correspond to the total angular momentum, its projection along the molecular axis, and the parity, respectively.

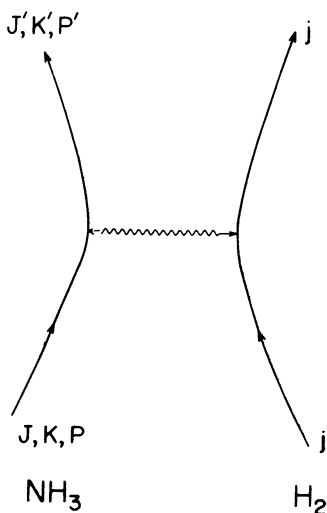


Fig. 1. The elementary process

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 \leftrightarrow 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,

$$V(r) = -\frac{1}{r^4} \left[\tilde{e} \cdot \tilde{Q} \cdot \tilde{\mu} - \frac{5}{2} (\tilde{e} \cdot \tilde{Q} \cdot \tilde{e}) (\tilde{e} \cdot \tilde{\mu}) \right]$$

where $\tilde{\mu}$ is the dipole moment of the polar molecule, \tilde{Q} is the quadrupole tensor of the H_2 molecule and $\tilde{e} = \tilde{r}/r$ 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 ν_p and ν_s and a low pressure (~ 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 ν_p (pump radiation with a power of ~ 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 ν_s (signal radiation with a power of $\sim 1 \mu\text{W}$) 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).

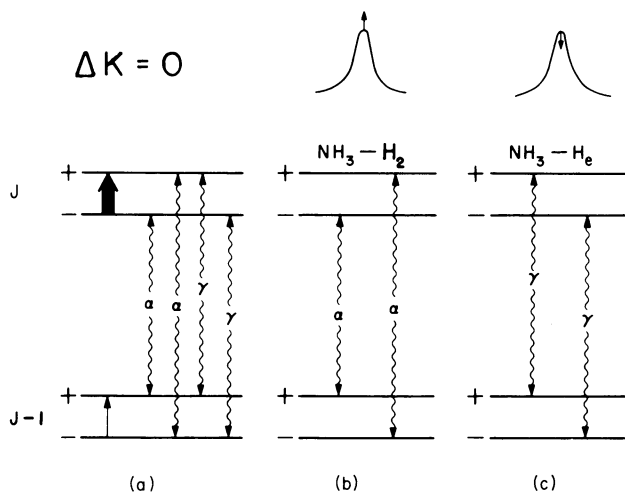


Fig.2 The four-level microwave double resonance experiments, for dipole-allowed transitions. The pump is shown by the bold arrow, the signal by the thin arrow, and the collision-induced transitions by wavy arrows. The H_2 molecule and the He atom act very differently as collision partners.

For the $\text{NH}_3 - \text{H}_2$ 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 $\text{NH}_3 - \text{He}$ 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 $\text{NH}_3 - \text{H}_2$ and the $\text{NH}_3 - \text{He}$ 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.

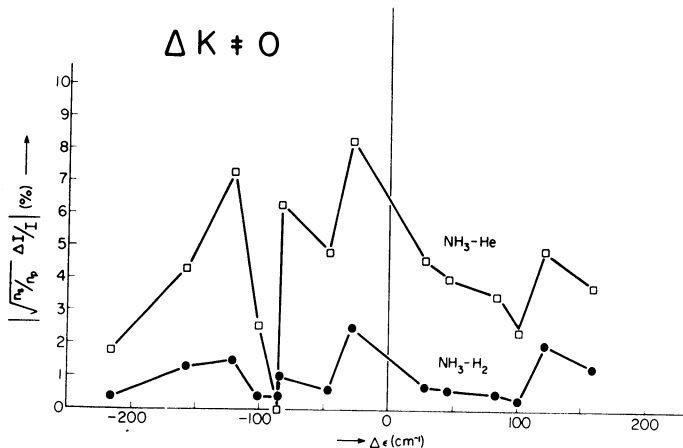


Fig.3. Results of four-level double resonance for dipole-forbidden transitions ($\Delta K=3n, n \neq 0$). Here the H_2 molecule and the He atom act very similarly on NH_3 as the collision partners.

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 $V(\underline{r})$ which can be rewritten (Oka 1973),

$$V(\underline{r}) = - \frac{8\sqrt{\pi^3}}{r^4} \mu Q \sum_{m_1, m_2, m} \begin{pmatrix} 1 & 2 & 3 \\ m_1, m_2, m \end{pmatrix} D_{0, m}^3(\Omega_r) D_{0, m_1}^1(\Omega_\mu) D_{0, m_2}^2(\Omega_Q)$$

where $D_{n, m}^l(\Omega)$ are rotation matrices for the spatial orientations Ω_r , Ω_μ , and Ω_Q of the position vector \underline{r} , the dipole moment $\underline{\mu}$, and the quadrupole moment \underline{Q} , respectively. It is seen from this formula that $\langle j | V(\underline{r}) | j \rangle = 0$ for $j=0$ because $\langle 0 | D_{0, m_2}^2(\Omega_Q) | 0 \rangle = 0$, 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.

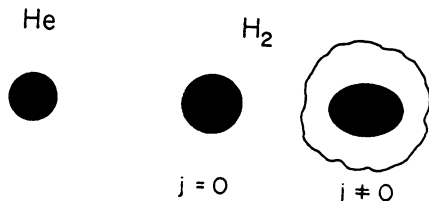


Fig.4. Models of the He atom and the H_2 molecule as collision partners.

4. PRESSURE BROADENING

The special characteristics of the 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 $j=0$ H_2 molecules in normal- H_2 and para- H_2 (18.4% in normal- H_2 and 73.2% in para- H_2 at dry ice temperature; 13.0% and 51.7% at room temperature). This can be used to distinguish the effect of the $j=0$ H_2 molecules from the rest. Figure 5 shows a recent measurement in the infrared region. A difference frequency laser

$NH_3:H_2$ (154 Torr, -66 C)

ν_1 $^oQ(3,3)$

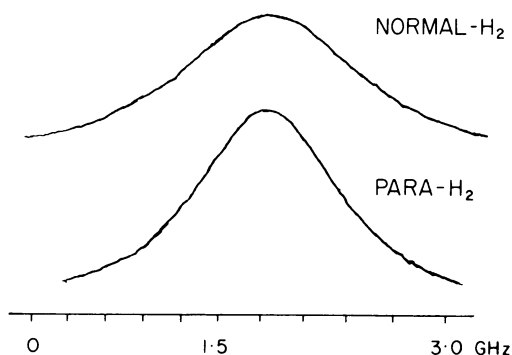


Fig.5. Pressure broadening of the infrared transition line ν_1 $^oQ(3,3)$ of NH_3 by normal- H_2 and para- H_2 at dry ice temperature. The total pressure is 154 torr for both traces. (D.R. Rao and T. Oka, 1979).

system was used as a frequency tunable infrared source. The difference between the normal- H_2 and para- H_2 as collision partners is clearly seen. Measurements in the infrared and microwave regions of NH_3 lines showed that the normal- H_2 containing more $J \neq 0$ H_2 is more effective as a perturber than the para- 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 $j \neq 0$ H_2 molecules have the same collision cross section as partners to NH_3 , we determine the ratio of the total collision cross section for the $j \neq 0$ H_2 to that for the $j=0$ 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 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 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 H_2 molecule considered as the collision partner is in the $j=0$ level or not. In the former case, the H_2 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- H_2) 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 H_2 $j=0$). 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 H_2 molecules in $j \neq 0$ levels act to reduce such population anomalies. This is because (a) the outer shell of such a H_2 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, Λ -type or inversion doubling. Thus for example the cooling mechanism proposed by Townes and Cheung (1969) for the $1_{10} \leftarrow 1_{11}$ transition of H_2CO is less likely to work for $j \neq 0$ H_2 because (a) the collision-induced $1_{10} \leftrightarrow 1_{11}$ transition will reduce the anomaly and (b) the required asymmetry in the rates of the $2_{11} \leftarrow 1_{11}$ and the $2_{12} \leftarrow 1_{10}$ transitions is less likely.

When the H_2 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- H_2 than para- H_2 (Black and Dalgarno 1976). The ratio of $j=0$ H_2 to the rest depends on how efficiently the mechanism of $H^+ + o-H_2 \leftrightarrow H^+ + p-H_2$ (Dalgarno, Black and Weisheit 1973) thermalizes the two species in the low temperature molecular cloud.

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 A.H. Black and A. Dalgarno, *Ap. J.* 203, 132 (1976).
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DISCUSSION FOLLOWING OKA

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

Oka: We boil off liquid H_2 then check the pureness of para- H_2 by observing the rotational Raman spectrum.

Thaddeus: You can buy pure para- H_2 . Presumably it is used by bubble chamber people.

Oka: Yes, but the trouble is that suppliers of liquid H_2 for bubble chambers sell only by tons.

Carruthers: I think that all of the Copernicus observations of interstellar H_2 are consistent with a thermal ortho to para-hydrogen ratio.

Oka: The circumstellar H_2 seems to be all thermalized, but the ratio for dark clouds is not known.

Townes: Have you 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 H_2CO . 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 H_2 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 H_2CO 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 NH_3 ?

Oka: The ratio is about 10 to 1. (Ap. J. Lett. 165, L15 (1971))

Winnewisser: Do collisions of $j=0$ H_2 and other H_2 affect differently the $K=1$ and 2 levels and the $K=3$ levels of NH_3 , 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 NH_3 . For $K=3$ transitions, that is, $k = \pm 1 \leftrightarrow \pm 2$ and $k = 3 \leftrightarrow 0$, 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 NH_3 - H_2 cross-sections for ortho and para- NH_3 ?

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- NH_3 and para- NH_3 , apart from the usual K -dependence.

Townes: I am a little puzzled. The conversion from ortho to para-NH₃ is presumably through the exchange reaction with protons, as is the case with H₂, although there may also be some other mechanism. In general it seems that NH₃ is approximately in thermal equilibrium, and that would seem to have some bearing on whether H₂ is also in thermal equilibrium.

Oka: I am surprised to hear that from you. Your initial measurement of NH₃ in Sgr B2 showed much higher intensity in the ortho lines than in the para lines.

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

Oka: A factor of two?

Townes: 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-NH₃. One consideration here is that the conversion between ortho and para-H₂ is expected to be slower than that between ortho and para-NH₃ or between spin modifications in other polyatomic molecules.

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

Oka: Even if NH₃ collides with neutral H₂, conversion can occur.

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

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

Townes: But surely the conversion occurs only by substitution?

Oka: Not necessarily. Ortho-para symmetry in polyatomic molecules is not as rigorous as in H₂. 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.

Townes: I thought that there is a laboratory experiment indicating that collisions with molecular hydrogen cannot vary the NH₃ 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 H₂ and D₂. In other words, nobody has yet produced in the laboratory anomalous spin populations of polyatomic molecules such as formaldehyde, water or NH₃.

Townes: 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 10¹⁵ collisions to accomplish conversion from ortho to para. Presumably for NH₃ 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 H₂ conversion, polyatomic molecules can convert much faster. I might mention that

Professor Curl and his collaborators attempted to make CH_4 molecules with anomalous spin modification ratio. They cooled CH_4 to He temperature, then boiled it suddenly, hoping that, in the same way as H_2 , the CH_4 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 CH_4 , 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 NH_3 where theory predicts much slower conversion. We could not detect an anomaly.

Field: I should just like to comment that in experiments involving $\tilde{\text{A}}^2\text{A}_1\text{NH}_2$ 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 NH_3 , so NH_3 is thermalized just as H_2 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 NH_3 , and therefore NH_3 conversion is at least as fast as H_2 conversion. Now if NH_3 spin modifications are not completely thermalized in interstellar space as observation seems to show, there is more possibility that H_2 spin modifications are not thermalized.

W. Watson: In exchanging the ortho and para forms of NH_3 , reactions of the form $\text{NH}_3 + \text{H}_3^+ \rightarrow \text{NH}_4^+ + \text{H}_2$, $\text{NH}_4^+ + \text{e} \rightarrow \text{NH}_3 + \text{H}$ 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- N_2 temperatures and my experiment goes down to dry ice temperature.

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