Collisional Transfer of Energy in Ammonia; Some Triple Resonance Experiments

Harold Jones * and Achim Eyer

Faculty of Physics, University of Freiburg, 78 Freiburg, West Germany

(Z. Naturforsch. **28 a**, 1703–1706 [1973]; received 19 July 1973)

Infrared-microwave-microwave triple resonance experiments in ammonia are reported. The power modulated P13 line of a N_2O laser was used to pump the ν_2[Q(8,7)] transition of ammonia. The dependance of the intensity of the collisionally induced signals produced at the (7,7), (6,6), (5,5) and (4,4) microwave transitions on c. w. microwave power applied to the (8,7) transition was measured. From the null signal observed for the (7,7) transition when the (8,7) transition was saturated, it was concluded that population changes produced in the (7,7) levels occur predominently via direct collisional transitions which are strongly parity sensitive and that other processes have little contribution. The signals observed for the (6,6), (5,5) and (4,4) are produced by processes which are largely insensitive to parity.

Introduction

We wish to report initial results of some infrared-microwave-microwave triple resonance experiments, carried out in the course of infrared-microwave double resonance investigations of collisional transfer of energy in ammonia.

The P13 line of the N_2O laser was first used to produce infrared-microwave double resonances in ammonia by Shimizu and Oka [1]. As a consequence of its close coincidence with the ν_2[Q(8,7)] transition of $^{14}NH_3$, irradiation of a sample of ammonia with this laser line causes a large increase in the (8,7) microwave absorption at 23,232.2 MHz. The effect of this laser radiation on other microwave transitions between levels not directly pumped by the laser, was observed [1] as small decreases in intensity of the (9,7) and (7,7) Stark modulated microwave absorption lines.

As a result of microwave-microwave double resonance experiments in pure ammonia, Oka [2] concluded that in the collisional transfer of energy, dipole selection rules (i. e. $\Delta J = 0, \pm 1$; $\Delta K = 0$ and parity change preferred over parity retention) predominate and that transitions in which $\Delta J > 1$ and $\Delta K \neq 0$ have much smaller probabilities.

Only two inversion doublets, the (7,7) and the (9,7) are connected to the laser-excited (8,7) level by a single-step transition obeying dipole selection rules. Using the more sensitive technique of infrared modulated infrared-microwave double resonance [3] we, in collaboration with Dr. W. A. Kreiner have observed collisionally induced signals in a total of 25 microwave transitions, some as far removed in quantum numbers from the excited (8,7) transition as the (1,1). Details of this work will be published elsewhere.

The fact that signals are observed at the various transition frequencies shows that the population difference between upper and lower levels of the microwave transitions are varying in phase with the laser chopping frequency. The source of this variation may be that "collisional selection rules" favour the transfer of population from one of the levels of the transition or in some non-selective process such as a "heating effect". The following triple resonance experiments were carried out to investigate the role played by selection rules in some of the observed signals.

Experimental

The experiments consisted of observing collisionally induced microwave signals produced when the chopped laser beam (1 KHz.) irradiated the ν_2[Q(8,7)] transition and then determining the effect of applying c.w. microwave power to the (8,7) transition. The (7,7), (6,6), (5,5) and (4,4) transitions were used as signal transitions.

The apparatus used consisted of a 3.5 metre K-band waveguide cell to which a vacuum tight "magic-T" coupler was attached. The cell was sealed

* Alexander-von-Humboldt Fellow.

Reprint requests to Dr. H. Jones, Fakultät für Physik der Universität Freiburg i. Br., *D-7800 Freiburg i. Br.*, Hermann-Herder-Straße 3.

at one end by a NaCl window, through which the chopped infrared radiation was admitted, and by a mica window at the other. The two microwave radiation fields were fed into the two arms of the "magic-T" through ferrite isolators. The microwave source in both cases was a frequency stabilised CSF carcinotron. In all cases the signal transition was at higher frequency that the (8,7) pumped transition and an adjustable waveguide cut-off was used to prevent the microwave pump radiation from reaching the detector diode. Observations were made using 500 mWatt average laser power, focused into the K-band cell by means of a BaF_2 lens. The maximum microwave pump power available in the cell was approximately 50 mWatt.

Results

The double resonance signal observed for the (7,7) transition with the microwave pump fully attenuated (20 dB), about 20 mTorr of ammonia and 10 microamps crystal current is shown in Figure 1 a. The resulting signals observed when 1 mWatt, 5 mWatt and 50 mWatt of microwave power, at the (8,7) transition frequency, was applied are shown in Figs. 1 b, 1 c and 1 d respectively. With the maximum microwave pump power the (7,7) signal reduced to very close to zero (Figure 1 d). The change in signal observed when the signal frequency was statibilsed at the line centre of the (7,7) microwave transition (25,715.14 MHz) and the unattenuated microwave pump was swept is shown in Figure 2.

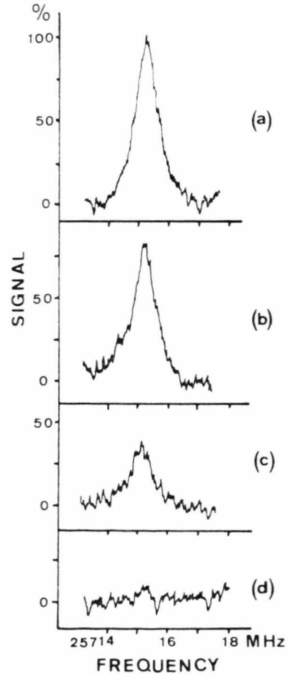

Fig. 1. Collisionally induced signals of the (7,7) microwave transition with approximately (a) 0 mWatt, (b) 1 mWatt, (c) 5 mWatt, (d) 50 mWatt of pump power at the (8,7) microwave transition frequency.

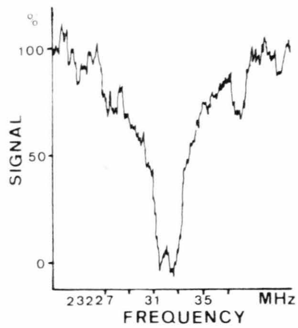

Fig. 2. Change in the (7,7) collisionally induced signal produced as the microwave pump is swept through the (8,7) transition frequency.

The minimum signal was obtained when the pump frequency was close to the centre of the (8,7) transition (23,232.2 MHz). When the ammonia pressure was increased to approximately 70 mTorr with the maximum pump power the signal only reduced to 30% of the unpumped peak height.

For the (4,4) transition (24,139.39 MHz) with 20 mTorr pressure an increase in signal strength of approximately 40% was observed on pumping the (8,7) transition. At higher pressures this change was very much reduced. For both the (5,5) and (6,6) transitions increases of the order of 20% were observed at pressures in the region of 20 mTorr when full microwave pumping power was applied to the (8,7).

Discussion

Some of the energy levels concerned are shown schematically in Figure 3. In the absence of micro-

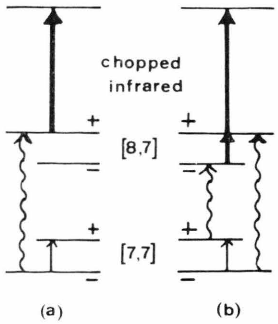

Fig. 3. Representation of some of the energy levels of ammonia. Radiation fields are shown by straight arrows, prefered collisional transitions are indicated by wavey arrows.

wave pumping power, (Fig. 3 a) the chopped laser output produces greatest population changes in the upper level of the (8,7) doublet. The strong signal observed at the (7,7) transition frequency (Fig. 1 a), which corresponds to a decrease in microwave absorption when the laser is pumping, is consistent with a decrease in population, caused by the laser, occuring mainly in the lower level of the (7,7) doublet, i.e. dipole selection rules having predominance. When microwave power is applied to the (8,7) transition (Fig. 3 b) the laser has a greater effect on the population of the lower level of the (8,7) doublet. This effect increases with increasing microwave power until when saturation is achieved population changes of equal magnitude are produced in the upper and lower levels of the (8,7) doublet, i.e. under these conditions the laser is exciting two levels of opposite parity.

With 50 mWatt of pump power at the (8,7) transition frequency the (7,7) signal reduces to very close to zero (Fig. 1 d), this power level in a K-band cell is probably sufficient to saturate the (8,7) transition when the pressure is 20 mTorr. The near zero signal observed shows that under these conditions the rates of transfer of population from the upper and lower levels of the (7,7) transition are almost equal. This shows that the (7,7) signal originates from a direct transfer process to the (8,7) which is strongly parity dependent, and that the contribution from any other source is small. It is not possible to differentiate between the contributions from "dipole" or "quadrupole" type transitions [2] in this experiment because both would react in a similar manner. Since the original double resonance signal corresponded to a decrease in microwave absorption this showed that the "dipole" type transitions have predominance and only this type of transition is indicated in Figure 3 b. The observation that at higher pressure the (7,7) signal did not completely disappear is probably due to incomplete saturation of the (8,7) microwave transition at this pressure.

For all the transitions (4,4), (5,5), (6,6) the observed double resonance signals correspond to a decrease in microwave absorption when the laser field is present. That is, a net decrease in the lower doublet level occurs. The parity of the inversion doublets of ammonia alternate with quantum number K. The levels of the (5,5) have the same parity as the (7,7) and the (8,7) but for the (4,4) and (6,6) the system is inverted. If parity was of importance in explaining the double resonance observations then parity retention ($+ \rightarrow +$) would have to predominate in the collisional transitions between the states $(8,7)_+$ and $(4,4)_+$ (or $(6,6)_+$), while parity change ($+ \rightarrow -$) would have to be favoured for those between $(8,7)_+$ and $(5,5)_-$. On applying the microwave pump to the (8,7) transition the lower ($-$) level is depleted. This produces an enhancement (20% to 40%) of the observed signals at the (4,4), (5,5) and (6,6) microwave transition frequencies, which corresponds to a further decrease in absorption beyond that present in the double resonance experiment. This is the opposite effect from that expected if parity was of importance in the production of these signals. It must therefore be concluded that the process that disturbes the Boltzmann distribution of these three doublets has little dependence on parity.

A non-specific effect such as the heating of the gas by the laser might account for these observations. The intensity of an absorption of a symmetric rotor is proportional to $T^{-5/2}$, see Reference [4]. (Where T is the observation temperature.) Temperature rises of 0.25 °C will thus produce a change in intensity of the microwave absorption lines of the order of -0.22%. If such a temperature change occurred in phase with the laser chopping, the resulting intensity change is of the right order of magnitude to account for the observed signals. It is difficult to know if under the experimental conditions an effective "temperature ripple" of amplitude 0.25 °C, oscillating at 1 KHz. is realistic or not.

Application of the microwave pump will increase the laser absorption, but only by approximately 0.2%, since the difference in population between the microwave levels is only about 0.4%. This effect alone is unlikely to account for the observed increase in signal of 20% to 40%.

The behaviour of a 3 level system under the influence of two strong, resonant radiation fields cannot be described in a closed form in general [5]. No attempt will be made here to give an exact treatment, but the following simple semi-classical approach may be useful to indicate a possible source of the observed increase. The infrared and microwave fields are assumed to saturate the relevant transitions. The population, n, of the microwave transition levels are assumed to be equal and the population of the upper level of the infrared transition is at first assumed to be negligible small. With only the infrared field present a change in population of 0.5 n is produced in the upper level of the microwave transition. When both fields are present a change of 0.33 n is produced in both of the levels of the microwave transition. Thus the total reduction of population in the ground state levels has increased from 0.5 n to 0.66 n i. e. a 32% increase.

This picture is, of course, much too simplified. "Hole burning" in the Doppler profile of the infrared transition occurs rather than complete saturation. This effect alone should not effect this estimation too greatly since the percentage increase when the microwave power is applied will be roughly that given above. An effect not considered which diminishes this change is the $\Delta J = 0$ "dipole" collisional transition, which tends to excite the lower level of the (8,7) in the absence of the microwave field. Oka [2] has shown that this collisional transition becomes important as "*K*" increases. However this estimation at least indicates a possible source of effects of the right order of magnitude.

Conclusions

The collisionally induced signal observed at the (7,7) results from direct transitions to the (8,7) levels which are strongly parity sensitive. The signals observed at the (4,4), (5,5) and (6,6) are produced by some process which is largely parity insensitive, possibly by a "heating effect".

Acknowledgements

We wish to gratefully acknowledge the support and interest of Prof. H. D. Rudolph in this work and to thank Dr. W. A. Kreiner for giving us great assistance over the optical parts of the equipment and for many discussions on the topic of collisional transfer of energy. We also wish to thank the Alexander-von-Humboldt Trust for the granting of a fellowship to one of us (H. J.) and to acknowledge financial support for this work by the Deutsche Forschungsgemeinschaft.

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