

## POSSIBLE ROTATIONAL EQUILIBRATION OF INTERSTELLAR AMMONIA BY RADIATIVE $\Delta k = \pm 3$ TRANSITIONS\*

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Received 1971 January 21

### ABSTRACT

It is pointed out that the probabilities of *radiative*  $\Delta k = \pm 3$  transitions between metastable rotational levels of ammonia are not much smaller than those for collision-induced transitions considered by Townes and his collaborators in the discussion of rotational relaxation of  $\text{NH}_3$  in interstellar space. Calculated values of the time of spontaneous emission for such radiative transitions give the upper limits of the lifetimes of metastable levels and provide a useful time standard in interstellar space. Competition between the radiative transitions and the collision-induced transitions are discussed; the discussion uses the calculated values of the former and the laboratory results on the latter. Lower limits for the density of collision partners required to comply with the observation by Cheung *et al.* are given.

### I. INTRODUCTION

Recently Cheung *et al.* (1969) have discussed relaxational processes between the metastable rotational levels ( $J = K$ ) of ammonia molecules observed in the region of Sgr B2. Various  $\Delta k = \pm 3$  transitions within the same spin modification (ortho  $k = 3n$  or para  $k = 3n \pm 1$ ) contribute to the relaxation. Cheung *et al.* considered only collision-induced transitions; they neglected radiative transitions because they thought that the electric-octopole transition, for which the radiation time is longer than the lifetime of the Universe, is the only radiative process to be considered. In this Letter we wish to point out that there are  $\Delta k = \pm 3$  *electric-dipole transitions* between the metastable levels and that the probabilities of these radiative transitions ( $\sim 10^{-9} \text{ sec}^{-1}$ ) are not much smaller than those of collision-induced transitions estimated by Cheung *et al.* (1969).

### II. THEORY

The possibility of  $\Delta k = \pm 3$  transition was first pointed out by Hanson (1967). The  $\Delta k = \pm 3$  transitions are normally forbidden, but, since they are not forbidden by spin symmetry, they become allowed as results of various state mixings through vibration-rotation interaction. Being an intramolecular interaction, the vibration-rotation interaction mixes various levels with the same  $J$ -value and the molecular symmetry. The relevant mixings with change of quantum numbers ( $\Delta k = \pm 2$ ,  $\Delta l = \mp 1$ ,  $\Delta v = 1$ ) (mixing I) and ( $\Delta k = \pm 1$ ,  $\Delta l = \pm 1$ ,  $\Delta v = 1$ ) (mixing II) are caused by the first-derivative terms from the expansion of the reciprocal inertia tensor in the vibration-rotation Hamiltonian (see for example, Oka 1967). Mixing I is caused by the term

$$H(\text{I}) = -2\pi B^2 a_t^{(yy)}(q_+ J_-^2 + q_- J_+^2)(c/h\nu_t)^{1/2},$$

and mixing II is caused by the term

$$H(\text{II}) = 2\pi i B C a_t^{(zz)}[(q_+ J_+ - q_- J_-)(J_z - \pi_z^*) + (J_z - \pi_z^*)(q_+ J_+ - q_- J_-)](c/h\nu_t)^{1/2}, \quad (1)$$

\* A part of this paper was presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1969.

where  $B$  and  $C$  are rotational constants,  $\nu_t$  is the frequency of a degenerate vibration,  $a_t^{(\alpha\beta)}$  is the first derivative of a component of the moment-of-inertia tensor  $I^{(\alpha\beta)}$  with respect to a normal coordinate  $Q_t$ , and  $q_{\pm}$  and  $J_{\pm}$  are vibrational and rotational operators, respectively.<sup>1</sup>

An example of the mixings is shown in Figure 1; the  $(J = 2, k = \pm 2)$  and the  $(J = 2, k = \mp 1)$  levels of  $\text{NH}_3$  in the ground vibrational state are mixed with the  $(J = 2, k = 0, l = \pm 1)$  level in the degenerate vibrational state  $v_t = 1$  through mixings I and II, respectively (several other mixings which also contribute to the weak transition are omitted in Fig. 1 for the sake of simplicity). As a result, the normally forbidden transitions  $(J = 2, k = \pm 2) \rightarrow (J = 1, k = \mp 1)$  become allowed by two kinds of intensity borrowing. The transitions can borrow intensity, first from the allowed vibrational transitions  $(J = 2, k = 0, l = \pm 1, v_t = 1) \rightarrow (J = 1, k = \mp 1, v = 0)$  through mixing I, and second from the allowed rotational transitions  $(J = 2, k = \pm 1) \rightarrow (J = 1, k = \pm 1)$  through mixings I + II. Since the rotational transition (caused by the permanent dipole moment  $\mu_c$ ) has a larger transition dipole moment than the vibrational transition (caused by the first derivative of dipole moment with respect to a normal coordinate  $Q_t$ ,  $\partial\mu_b/\partial Q_t$ ), the contributions of the two types of intensity borrowing to the weak transition are of the same order of magnitude in spite of the fact that the latter

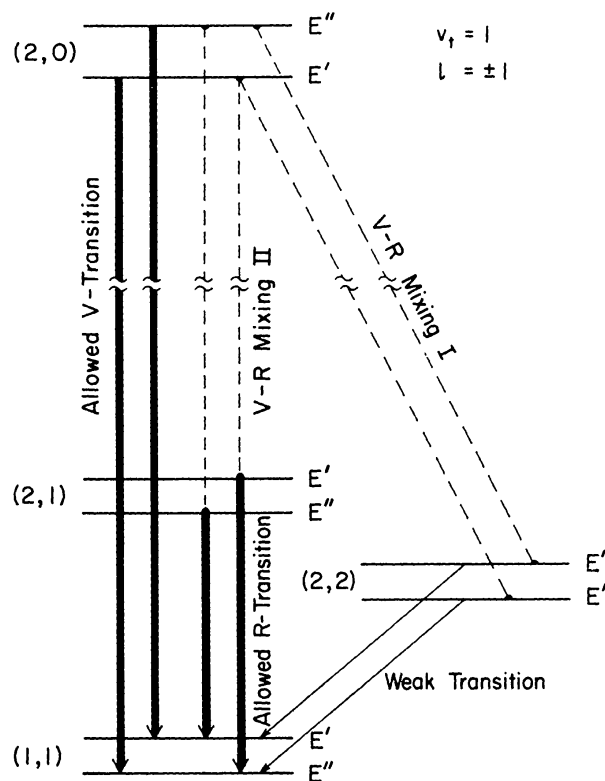


FIG. 1.—An example of mixings due to vibration-rotation interaction and resulting intensity borrowing from allowed vibrational and rotational transitions. The upper pair of rotational levels ( $J = 2, k = 0$ ) is in the excited state of a degenerate vibration  $v_t = 1, l = 1$ ; and the three lower pairs of rotational levels  $(2,1)$ ,  $(2,2)$ , and  $(1,1)$  are in the ground vibrational levels. The weak transitions  $(2,2) \rightarrow (1,1)$  borrow intensity from the allowed vibrational transitions through the first-order mixing (vibration-rotation mixing I) and from the allowed rotational transitions through the second-order mixing (mixings I + II).

<sup>1</sup> The subscript 1 indicating a component of the degenerate vibration  $\nu_t$  is omitted throughout this paper.

borrowing is through second-order mixing. The transition dipole moment induced by these mixings is indeed very small compared with those for normally allowed transitions, but the resultant transition probabilities are comparable with those for collisional processes in interstellar space. In this respect it should be remembered that in the ammonia spectrum, even the effect of  $\Delta k = \pm 6$  mixing, which is of higher order than the  $\Delta k = \pm 3$  mixing here under consideration, is large enough to be observable as a frequency shift (Strandberg *et al.* 1947; Nielsen and Dennison 1947).

We have worked out the detailed theory of such transitions and have found that the square of the dipole matrix element for the  $(J, k + 3) \rightarrow (J - 1, k)$  transition summed over the three perpendicular directions in space is expressed as (Watson 1971)

$$|\mu_{ij}|^2 = \left[ \sum_t \frac{B^2 a_t^{(bb)}}{\nu_t^2} \left( \frac{a_t^{(bc)}}{I_{cc} - I_{bb}} \mu_c - \frac{\partial \mu_b}{\partial Q_t} \right) \right]^2 F(J, k), \quad (2)$$

where

$$F(J, k) = (J + k)(J + k + 1)(J + k + 2)(J + k + 3) \\ \times (J - k - 1)(J - k - 2)/J(2J + 1). \quad (3)$$

The summation in equation (2) extends over all the degenerate vibrations  $t$ . The first term in equation (2) represents the intensity borrowing from the rotational transition; the second term, that from the vibrational transition.

### III. CALCULATION

Among the various quantities appearing in equation (2), the values of  $B$ ,  $\nu_t$ ,  $I_{cc}$ ,  $I_{bb}$ ,  $\mu_c$ , and  $\partial \mu_b / \partial Q_t$  have been determined experimentally for  $\text{NH}_3$ , and  $a_t^{(bc)}$  and  $a_t^{(bb)}$  have been calculated from a normal coordinate calculation. The following values were used;  $B = 9.9443 \text{ cm}^{-1}$ ,  $I_{bb} = 1.6957 \text{ amu}A^2$ ,  $I_{cc} = 2.7215 \text{ amu}A^2$ ,  $\nu_3 = 3444 \text{ cm}^{-1}$ ,  $\nu_4 = 1627 \text{ cm}^{-1}$  (Benedict and Plyler 1957),  $\mu_c = 1.468 \text{ debye}$  (Coles *et al.* 1951),  $\partial \mu_b / \partial Q_3 = 0.1857$ ,  $\partial \mu_b / \partial Q_4 = 0.5402$  [in  $(\text{amu}A^2)^{-1/2} \text{ debye}$ ] (McKean and Schatz 1956),  $a_3^{(bb)} = -1.056$ ,  $a_3^{(bc)} = -0.813$ ,  $a_4^{(bb)} = 1.242$ , and  $a_4^{(bc)} = -0.691$  [in  $(\text{amu}A^2)^{1/2}$ ] (Morino, Kuchitsu, and Yamamoto 1968). The uncertainties of  $B$ ,  $I_{bb}$ ,  $I_{cc}$ ,  $\nu_3$ ,  $\nu_4$ , and  $\mu_c$  are negligible compared with those of the other quantities. Since reliable normal coordinates are known for  $\text{NH}_3$ , the uncertainties of the  $a_t^{(\alpha\beta)}$  are estimated to be less than 10 percent. The accuracy of the values of  $\partial \mu_b / \partial Q_t$  are quoted by the authors to be about 10 percent. The only ambiguity in the calculation is caused by the lack of information on the relative sign of  $a_t^{(bc)} \mu_c (I_{cc} - I_{bb})^{-1}$  and  $\partial \mu_b / \partial Q_t$  in equation (2). Since the magnitudes of these terms are of the same order, the ambiguity is serious for the calculation of transition probabilities. We have inferred the relative sign of these quantities by using a simple model in which a positive charge is placed on the hydrogen atoms and a negative charge on the nitrogen atom; this model gives the same sign for the two terms, and thus the effects of rotational and vibrational intensity borrowing enhance each other. Using these numbers, we calculate the values of the expression in the brackets in equation (2) to be  $6.2 \times 10^{-5} \text{ debye}$ . (In case the relative sign of the two terms inferred above is incorrect, the value is  $1.2 \times 10^{-5} \text{ debye}$ .)<sup>2</sup>

The lifetimes  $t$  of the metastable levels due to spontaneous emission have been calculated from

$$\frac{1}{t} = \frac{4\omega^3}{3\hbar c^3} |\mu_{ij}|^2 \quad (4)$$

(see for example, Townes and Schawlow 1955) and are listed in Table 1. Also for possible

<sup>2</sup> The experimental determination of the sign of  $\partial \mu_b / \partial Q_t$  relative to  $\mu_c$  by the use of vibration-rotation intensity perturbation is highly desired.

TABLE 1  
CALCULATED TIME FOR SPONTANEOUS EMISSION  $t$  AND  
ABSORPTION COEFFICIENT  $\gamma$  AT ROOM TEMPERATURE

Transition	$\nu(\text{cm}^{-1})$	$t(10^9 \text{ sec})$	$\gamma(10^{-7} \text{ cm}^{-1})^*$
(2,2)→(1,1) . . . . .	28.53	7.32	0.06
(3,3)→(2,0) . . . . .	25.93	1.37	0.9
(4,4)→(3,1) . . . . .	23.36	0.69	0.9
(5,5)→(4,2) . . . . .	20.80	0.50	1.2
(6,6)→(5,3) . . . . .	18.25	0.44	2.4

\* Pressure-broadening parameter  $\Delta\nu_p$  of  $30 \text{ MHz torr}^{-1}$  is used for the calculations.

future laboratory detection of these transitions, the approximate absorption coefficients  $\gamma$  at room temperature are given in the same table.<sup>3</sup>

Unlike normal rotational transitions, the weak transitions occur between the upper components and between the lower components of a pair of inversion-doublet levels (see Fig. 1); therefore, they should be observed as a very closely spaced doublet of equal intensity. The (3,3) → (2,0) transition is exceptional in that the lower component of the (2,0) levels is absent because of the exclusion principle and the transition occurs only between the upper components. The implication of this in regard to rotational equilibration of  $\text{NH}_3$  is discussed later. It should be noted that all the  $\Delta k = 3$  transitions listed in Table 1 occur between levels of the same spin modification of the molecule. The ortho ( $k = 3n$ ) ↔ para ( $k \neq 3n$ ) transitions which are caused by mixing due to small nuclear-spin-rotation term are several orders of magnitude slower than those listed in Table 1.

#### IV. DISCUSSION

The radiative lifetimes shown in Table 1 give the upper limits of the lifetimes of the metastable levels and provide a useful time standard for ammonia in interstellar space. Depending on whether the radiative transitions are faster or slower than collision-induced transitions, the former or the latter play a dominant role in the rotational equilibration in interstellar space. If the radiative transitions are faster than the collision-induced transitions and the radiation temperature is low as normally assumed, the effective temperature of the (3,3) inversion doublet should be very low because the radiative transition (3,3) → (2,0) depletes molecules in the upper component of the (3,3) inversion-doublet level. The observation of Cheung *et al.* that the (3,3) emission line is normally rather strong means that the slow radiative process is negligible compared with the collisional pumping of molecules from the lower component to the upper component of the inversion doublet ( $\Delta J = \Delta k = 0$ ,  $\beta$ -transition). Using the observed temperature of the order of  $100^\circ \text{ K}$  and the radiative lifetime of the (3,3) level given in Table 1, we can set an upper limit of the order  $10^7 \text{ sec}$  to the time for the  $\beta$ -transition. Also, the results in Table 1 show that the spontaneous emission (3,3) → (2,0) is much faster than the (2,2) → (1,1) and therefore that spontaneous emission would tend to produce a distribution opposite to that observed. Therefore, unless there is much more ortho- $\text{NH}_3$  than para- $\text{NH}_3$  in the cloud by some reason,<sup>4</sup> we have to conclude that the collision-

<sup>3</sup>  $Q$ -type  $\Delta k = \pm 3$  transitions may be more convenient for laboratory detection; the dipole matrix elements of the  $Q$ -type transitions are given by same formula as equation (2) except that the following  $F(J, k)$  should be used:

$$F(J, k) = (J + k + 1) (J + k + 2) (J + k + 3) (J - k) (J - k - 1) \\ \times (J - k - 2) / J(J + 1).$$

<sup>4</sup> This could be the case if ammonia molecules in the cloud are formed by rapid evaporation from the surface of low-temperature dust grains.

induced  $\Delta k = \pm 3$  transitions are faster than the radiative  $\Delta k = \pm 3$  transitions, as initially discussed by Cheung *et al.* (1969).<sup>5</sup>

These considerations, together with laboratory results on collision-induced transitions, can set a lower limit to the number of collision partners in the cloud. Three types of collision-induced transitions have to be considered: the  $\beta$ -transition ( $\Delta J = 0, \Delta k = 0$ ), the  $\alpha$ -transition ( $\Delta J = 1, \Delta k = 0$ ) and the  $\phi$ -transition ( $\Delta k = \pm 3$ ). The laboratory results on the probabilities of these transitions and the pressure-broadening parameters (Smith and Howard 1950) are summarized as follows:

i)  $\text{NH}_3\text{-He}$  collision:  $\phi \sim \alpha \gtrsim 0.1\beta$  (Oka 1968) ,

$$\Delta\nu_p \sim 1.3 \text{ MHz torr}^{-1} ;$$

ii)  $\text{NH}_3\text{-H}_2$  collision:  $\phi < 0.1\alpha \sim 0.01\beta$  (Daly and Oka 1970) ,

$$\Delta\nu_p \sim 3.0 \text{ MHz torr}^{-1} .$$

In both cases the  $\beta$ -transition is by far the fastest (essentially because of the smallness of transferred energy); the value of  $\Delta\nu_p$  can be used therefore to estimate the probability of the  $\beta$ -transition. Then by using the relations given above, the time for the  $\phi$ -transition ( $\Delta k = \pm 3$ ) which equilibrates the metastable levels is calculated to be  $5 \times 10^{10}/n_{\text{He}}$  sec and  $2 \times 10^{11}/n_{\text{H}_2}$  sec for  $\text{NH}_3\text{-He}$  collisions and for  $\text{NH}_3\text{-H}_2$  collisions, respectively, where  $n_{\text{He}}$  and  $n_{\text{H}_2}$  are the densities of the collision partners. In the case of  $\text{NH}_3\text{-H}_2$  collisions, no  $\Delta k = \pm 3$  transitions have been observed in the laboratory experiment (Daly and Oka 1970) and  $2 \times 10^{11}/n_{\text{H}_2}$  sec gives the lower limit of the time of  $\Delta k = \pm 3$  transitions. The condition that the collision-induced  $\Delta k = \pm 3$  transitions are faster than the corresponding radiative transitions then sets the lower limit to the density of the collision partners  $n_{\text{He}} > 50 \text{ cm}^{-3}$  or  $n_{\text{H}_2} > 200 \text{ cm}^{-3}$ . The estimated value of  $n_{\text{H}_2} \sim 1000$  of Cheung *et al.* (1969) obtained from the consideration of competition between the radiative and collision-induced  $\beta$ -transition ( $\Delta J = 0, \Delta k = 0$ ) satisfies the condition given above.

Finally, we wish to point out that the weak radiative rotational transitions discussed in this paper exist for any molecule that does not have a center of symmetry. Thus, for example, methane can equilibrate with a radiational environment through such transitions.

We wish to thank G. Herzberg and P. R. Bunker for critical reading of the paper.

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<sup>5</sup> The observation of Cheung *et al.* (1969) that the (1,1) radiation extends farther toward the rim of the cloud than the (3,3) radiation probably means that the radiative transitions are more important in the outer area of the cloud.