ROTATIONAL LINE STRUCTURE IN THREE-PHOTON SCATTERING BY SYMMETRIC TOP MOLECULES

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A first fine structure study of rotational three-photon scattering by symmetric top molecules is performed using angular momentum and irreducible spherical tensor methods. Rotational line intensities are calculated for NH_3 —— a case accessible to observation by available spectroscopic laser technique.

Three-photon scattering (TPS) of laser light is a new effect now under study theoretically and experimentally [1–3]. Maker [4] pointed to the feasibility of fine observations of TPS lines due to rotational motions in the scattering gases, and performed calculations and experimental observations for *spherical* top molecules of methane under pressure. Here, the problem is dealt with for *symmetric* top molecules, and line intensities are calculated for NH_3.

For light linearly polarized along Z and propagating along Y, the intensity components of the spectral line scattered at frequency $2\omega + \omega_R$ into a unit body angle in the X-direction is:

$$I_n^{2\omega \pm \omega_R} = \frac{2\pi(2\omega \pm \omega_R)^4}{c^5} I_0^2 g_I N_{JK} \frac{1}{2J+1} \sum_{MM'} \left| \left(b_{nZZ}^{2\omega} \right)_{J K M}^{J'K'M'} \right|^2, \tag{1}$$

where $n = Y$, or $n = Z$. Above, JKM and $J'K'M'$ define the initial and final rotational state, $\omega_R = \hbar^{-1} |E(J',K') - E(J,K)|$, I_0 is the incident laser light intensity, g_I the nuclear statistical weight, and N_{JK} the number of molecules in the initial state.

The matrix elements of the non-linear molecular polarizability operator b_{nZZ} in (1) are readily calculated by transformation into spherical tensors B_m^l, as:

$$b_{ZZZ} = -i\sqrt{\tfrac{3}{5}} B_0^1 + i\sqrt{\tfrac{2}{5}} B_0^3, \qquad b_{YZZ} = (1/\sqrt{30})(B_1^1 + B_{-1}^1) - \sqrt{\tfrac{2}{15}}(B_1^3 + B_{-1}^3). \tag{2}$$

Since the transformation coefficients of spherical tensors and the rotational wave functions depend on Wigner functions, use can be made of the formula [5]:

$$\left| \left(B_m^l \right)_{J K M}^{J'K'M'} \right|^2 = (2J'+1)(2J+1) \begin{pmatrix} J' & l & J \\ -K' & q' & K \end{pmatrix}^2 \begin{pmatrix} J' & l & J \\ -M' & m & M \end{pmatrix}^2 \left| \tilde{B}_{q'}^l \right|^2, \tag{3}$$

where the tilde denotes a tensor in molecular coordinates. On summation over M and M', the following general expression results for the Z-component of TPS line intensity:

$$I_Z^{2\omega \pm \omega_R} = \frac{2\pi(2\omega \pm \omega_R)^4}{35\,c^5} I_0^2 g_I N_{JK} (2J'+1) \left\{ 7 \begin{pmatrix} J' & 1 & J \\ -K' & q' & K \end{pmatrix}^2 \left| \tilde{B}_{q'}^1 \right|^2 + 2 \begin{pmatrix} J' & 3 & J \\ -K' & r' & K \end{pmatrix}^2 \left| \tilde{B}_{r'}^3 \right|^2 \right\}. \tag{4}$$

That for the Y-component is similar, with the first term multiplied by $\frac{1}{9}$ and the second by $\frac{2}{3}$. The line intensity depends on the parameters $|\tilde{B}_{q'}^1|^2$ and $|\tilde{B}_{r'}^3|^2$, which account for the non-linear properties and symmetry of the molecule. For the symmetry C_{3v}, the general formula (4) becomes:

$$I_Z^{2\omega \pm \omega_R} = \frac{2\pi}{c^5}(2\omega \pm \omega_R)^4 N I_0^2 F(J,K), \tag{5}$$
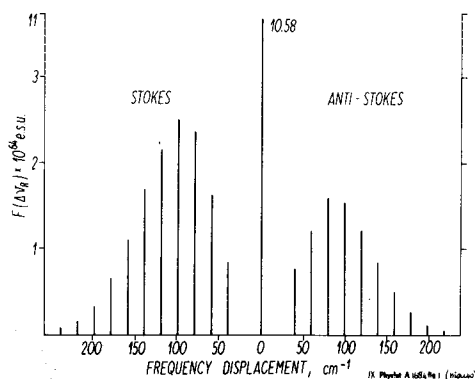
Fig. 1. The TPS rotational structure $F(\Delta\nu_R)$ for NH_3 molecules.

where we have introduced the TPS rotational structure factor:

$$F(J,K) = \frac{g_I}{140} \left[\frac{B^2 A h^3}{\pi(kT)^3}\right]^{1/2} \exp\left[\frac{-BJ(J+1)-(A-B)K^2}{kT}\right] \tag{6}$$

$$\times (2J+1)\left\{7\left|\widetilde{B}_0^1\right|^2 (2J'+1)\begin{pmatrix} J' & 1 & J \\ -K' & 0 & K \end{pmatrix}^2 + 2\left|\widetilde{B}_0^3\right|^2 (2J'+1)\begin{pmatrix} J' & 3 & J \\ -K' & 0 & K \end{pmatrix}^2 + \right.$$

$$\left. + 2\left|\widetilde{B}_3^3\right|^2 (2J'+1)\begin{pmatrix} J' & 3 & J \\ -K' & 3 & K \end{pmatrix}^2 + 2\left|\widetilde{B}_{-3}^3\right|^2 (2J'+1)\begin{pmatrix} J' & 3 & J \\ -K' & -3 & K \end{pmatrix}^2\right\}$$

with parameters:

$$\left|\widetilde{B}_0^1\right|^2 = \frac{3}{5}\left(b_{333}^{2\omega} + 2b_{113}^{2\omega}\right)^2, \qquad \left|\widetilde{B}_0^3\right|^2 = \frac{2}{5}\left(b_{333}^{2\omega} - 3b_{113}^{2\omega}\right)^2, \qquad \left|\widetilde{B}_{-3}^3\right|^2 = \left|\widetilde{B}_3^3\right|^2 = 2\left(b_{111}^{2\omega}\right)^2. \tag{7}$$

Summation in (5) over all J and K and over the permitted transitions yields the following total intensity of elastic TPS:

$$I_Z^{2\omega} = \frac{N\pi(2\omega)^4}{70c^5} I_0^2 \left\{7\left|\widetilde{B}_0^1\right|^2 + 2\left|\widetilde{B}_0^3\right|^2 + 4\left|\widetilde{B}_3^3\right|^2\right\}. \tag{8}$$

This expression is a particular case of a formula previously derived by Kielich [1].

The TPS lines are due to quantum transitions obeying the selection rules: $\Delta J = 0, \pm 1, \pm 2, \pm 3$; $\Delta K = 0, \pm 3$. The values of the molecular constants A and B of eq. (6) assumed for NH_3 in our calculations are [6]: $A = 189 \times 10^9$, $B = 298 \times 10^9$ in Hz; the hyper-polarizability tensor elements in (7) are [7]: $b_{333} = -13.176 \times 10^{-32}$, $b_{113} = -2.646 \times 10^{-32}$, $b_{111} = 1.323 \times 10^{-32}$ in $cm^5/e.s.u.$. Fig. 1 is a calculated graph of the function $F(\Delta\nu_R)$ —— the sum of the factors $F(J,K)$, contributing to the intensity of lines shifted by the same amount ν_R with regard to 2ν.

[1] S. Kielich, Physica 30 (1964) 1717; Acta Phys. Polonica 26 (1964) 135; J. Physique 28 (1967) 519;
[2] R.W. Terhune, P.D. Maker and C.M. Savage, Phys. Rev. Lett. 14 (1965) 681;
    P.D. Maker, Phys. Rev. 1 (1970) 923, and references therein.
[3] D.A. Long and L. Stanton, Proc. Roy. Soc. London 318A (1970) 441.
[4] P.D. Maker, in: Physics of quantum electronics (Mc. Graw-Hill, New York, 1966) p. 60.
[5] V.B. Berestetskii, E.M. Liftshitz and L.P. Pitaevskii, Relativistic quantum theory (Pergamon Press, 1971) Part I.
[6] C.H. Townes and A.L. Schawlow, Microwave spectroscopy (Mc Graw-Hill, New York, 1955).
[7] N.S. Hush and M.L. Williams, Theor. Chim. Acta 25 (1972) 346.