ROTATIONAL HYPER-RAMAN LIGHT SCATTERING BY AXIAL MOLECULES WITHOUT A CENTRE OF INVERSION

By T. BANCEWICZ, Z. OŻGO AND S. KIELICH

Institute of Physics, A. Mickiewicz University, Poznań*

In terms of spherical tensors and Wigner 3-j coefficients, calculations are performed of the intensities of rotational lines in hyper-Raman scattering spectra. Using available values of hyperpolarizability tensor elements, numerical calculations are made of intensities related with rotational transitions for the molecules NO, CO, HF and NH_3.

The shape of the spectrum depends strongly on the sign and value of hyperpolarizability tensor elements and thus can serve for checking the ab initio calculated values of the tensor elements. The intensity distribution in the spectrum depends on molecular parameters $|\tilde{B}_m^l|^2$ tabulated in the paper as functions of the Cartesian hyperpolarizability tensor elements for linear and symmetric top molecules.

1. Introduction

Interaction between a molecule and light of high intensity leads to processes of many--photon light scattering [1]. Since the scattering molecules perform rotational and vibrational motions, lines disposed in the neighbourhood of the successive harmonics emerge in the scattered spectrum. The earliest observations of nonlinear light scattering were performed by Terhune et al [2] on molecules without a centre of symmetry in conformity with theoretical predictions [3, 4]. The phenomenon in which the second-harmonic frequency of scattered radiation is modulated by frequencies of eigen-vibrations of the scattering molecule is currently referred to as vibrational hyper-Raman light scattering [5–7]. In the particular case when contributions from molecular motions are not apparent in the spectrum and the scattered frequency is exactly the double of the incident frequency, the process is termed hyper-Rayleigh scattering [5–8]. Rotational molecular motions give rise to a fine structure of the spectral line in both these types of scattering usually observed in the form of rotational broadening of the line [9]. The rotational fine structure of a hyper-Rayleigh line is sometimes referred to as the rotational hyper-Raman spectrum. The first observations of a spectrum of this type in compressed gaseous methane are due to Maker [10], who moreover proposed a theory of the effect for spherical top molecules. The problem is

* Address: Zakład Optyki Nieliniowej, Instytut Fizyki, Uniwersytet im. A. Mickiewicza, Grunwaldzka 6, 60-780 Poznań, Poland.

solved for the case of linear and symmetric top molecules by the authors of Refs [11–14].

In this paper, by having recourse to spherical tensors and 3-j Wigner coefficients, the intensities of rotational lines are calculated for axial molecules. Numerical calculations for NO, CO, HF and NH_3 point to more advantageous observation conditions of rotational hyper-Rayleigh structure for these molecules than for methane.

From the formulas derived by us for the intensities, the line strengths of the transitions $JK \to J'K'$ and $J'K' \to JK$ are found to be equal to each other, as in linear scattering. Also, the depolarization ratios for the lines corresponding to the two transitions are mutually equal.

Relations between the molecular parameters $|\tilde{B}_m^l|^2$ introduced in this paper and the hyperpolarizability tensor elements $b_{\alpha\beta\gamma}^{2\omega}$ in Cartesian co-ordinates for the various symmetries, as well as the analytic forms of the 3-j Wigner coefficients for numerical calculations obtained from the formulas of Jucis [15], are given in Appendices A and B.

The problem has been recently discussed by similar methods for the case of linear scattering by Altman and Strey [16] in the electric dipole approximation, and by Ying-Nan Chiu [17] taking into consideration magnetic dipole and electric quadrupolar terms.

2. Theory

In a molecular system, acted on by the intense electric field $E(t) = E^0 \cos \omega t$ of a light wave vibrating at the circular frequency ω, the electric moment induced is quite generally a nonlinear function of $E(t)$. In this paper, we restrict our considerations to the nonlinear dipole moment induced at doubled incident frequency 2ω [3]:

$$m_i^{2\omega}(t) = \tfrac{1}{4} b_{ijk}^{2\omega} E_j^0 E_k^0 \cos 2\omega t,$$

where $b_{ijk}^{2\omega}$ is the tensor of second-order nonlinear molecular polarizablity often referred to as the molecular hyperpolarizability tensor. This induced moment of order 2 defines Rayleigh scattering at the frequency 2ω, referred to as hyper-Rayleigh scattering.

At scattered light observation performed at right angles (90°) to the propagation direction of the incident beam, the total scattered intensity can be divided into two components: a vertical component V, and a horizontal one H, defined in relation to the plane of observation. We restrict our calculations to V_v and H_v for the case of vertically polarized incident light, since in the electric dipole approximation no additional information is gained from horizontal polarization because the Krishnan relation $H_v = V_h = H_h$ holds (lower indices v, h describe the state of polarization of the incident wave).

Similarly as for usual Raman scattering [18, 19], the intensities of the spectral lines of either component of scattered radiation with the frequencies $2\omega + \omega_{n'n}$ are given by the formulas [11]:

$$V_v^{2\omega+\omega_{n'n}} = \frac{2\pi}{c^5} (2\omega+\omega_{n'n})^4 I_0^2 g_{I,K} \frac{N_n}{d_n} \sum |(b_{vvv}^{2\omega})_{nl}^{n'k}|^2, \tag{1a}$$

$$H_v^{2\omega+\omega_{n'n}} = \frac{2\pi}{c^5} (2\omega+\omega_{n'n})^4 I_0^2 g_{I,K} \frac{N_n}{d_n} \sum |(b_{hvv}^{2\omega})_{nl}^{n'k}|^2, \tag{1b}$$

where $\omega_{n'n}$ is the frequency of the vibrational-rotational transition $n \to n'$ of the molecule; I_0 — the laser radiation intensity; $g_{I,K}$ — the nuclear statistical weighting factor; N_n — the number of molecules in the initial state; d_n — the degeneracy multiplicity for the initial state; i and k label the degenerate states of the initial level n and final level n', and summation extends over all possible combinations of states between the initial and final levels.

In order to express the scattered intensity in terms of molecular parameters, we perform a transformation of the hyperpolarizability tensors $b_{ijk}^{2\omega}$, defined in laboratory co-ordinates, to molecular co-ordinates according to the law:

$$b_{ijk}^{2\omega} = c_{i\alpha}c_{j\beta}c_{k\gamma}\tilde{b}_{\alpha\beta\gamma}^{2\omega}, \tag{2}$$

where the transformation coefficients $c_{i\alpha}$ have the meaning of cosines of the angles between the laboratory axes "i" and molecular axes "α".

By (2), the matrix elements occurring in Eqs (1a) and (1b) can be written in the form of products of two integrals:

$$(b_{ijk}^{2\omega})_n^{n'} = \int \psi_{v'}^* \tilde{b}_{\alpha\beta\gamma}^{2\omega} \psi_v dQ \int \psi_{R'}^* c_{i\alpha} c_{j\beta} c_{k\gamma} \psi_R d\tau. \tag{3}$$

The first integral describes hyper-Rayleigh and vibrational hyper-Raman scattering, whereas the second integral accounts for the rotational structure. The hyperpolarizability tensor $\tilde{b}_{\alpha\beta\gamma}^{2\omega}$ depends parametrically on the normal vibrational co-ordinates Q_n of the molecule. Since deviations of the nuclei from their equilibrium positions are small, each of the tensor elements $\tilde{b}_{\alpha\beta\gamma}^{2\omega}$ can be expanded in a series in those co-ordinates [3]:

$$\tilde{b}_{\alpha\beta\gamma}^{2\omega}(Q) = \tilde{b}_{\alpha\beta\gamma}^{2\omega}(0) + \sum_n \left(\frac{\partial \tilde{b}_{\alpha\beta\gamma}^{2\omega}}{\partial Q_n}\right)_0 Q_n + \frac{1}{2}\sum_{nm} \left(\frac{\partial^2 \tilde{b}_{\alpha\beta\gamma}^{2\omega}}{\partial Q_n \partial Q_m}\right)_0 Q_n Q_m + \dots$$

In this paper, we restrict our considerations to the rotational structure of the hyper-Rayleigh line and thus shall take the first term, independent of the Q_n, only.

The calculation of a matrix element between two rotational states from the product of three directional cosines is simplified by having recourse to a spherical representation of the hyperpolarizability tensor, since now the rotational wave functions for symmetric top molecules as well as the transformation coefficients of spherical tensors are expressed in terms of Wigner functions $D_{KM}^{(J)}(\alpha, \beta, \gamma)$ [20]:

$$\psi_{JKM}(\alpha, \beta, \gamma) = i^{J-K} \sqrt{\frac{2J+1}{8\pi^2}} \, D_{KM}^{(J)}(\alpha, \beta, \gamma), \tag{4}$$

$$B_m^l = \sum_{m'} D_{m'm}^{(l)}(\alpha, \beta, \gamma)\tilde{B}_{m'}^l. \tag{5}$$

The Euler angles α, β, γ define the mutual position of the molecular and laboratory co-ordinate systems.

The Cartesian elements of the hyperpolarizability tensor can be expressed as the following linear combinations of spherical tensors:

$$b_{\alpha\beta\gamma} = \sum_{klm} c_{\alpha\beta\gamma}^{klm} B_m^{l,k}, \tag{6}$$

.

where l, m define, respectively, the rank and element of the spherical tensor, whereas the index k is introduced by us to distinguish different tensors of the same rank occurring in the sum (6). The coefficients $c_{\alpha\beta\gamma}^{klm}$ are available in tabulated form in Maker's paper [9].

The intensity of hyper-Raman scattering from the rotational transition $JK \to J'K'$ is given by the line strength of the transition:

$$S_{k=v,h}(JK, J'K') = \sum_{MM'} |(b_{kvv}^{2\omega})_{JKM}^{J'K'M'}|^2. \tag{7}$$

With regard to the transformation (6), the formula:

$$\iiint D_{m'_1 m_1}^{(j_1)}(\omega) D_{m'_2 m_2}^{(j_2)}(\omega) D_{m'_3 m_3}^{(j_3)}(\omega) \frac{d\omega}{8\pi^2} = \begin{pmatrix} j_1 & j_2 & j_3 \\ m'_1 & m'_2 & m'_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}, \tag{8}$$

and the orthogonality conditions for Wigner 3-j coefficients:

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} = \frac{\delta_{j_3 j'_3}\delta_{m_3 m'_3}}{2j_3 + 1}, \tag{9}$$

we obtain the following expressions for the line strengths of the intensity components (1a) and (1b), respectively:

$$S_v(JK, J'K') = (2J+1)(2J'+1)\left\{\frac{1}{5}\begin{pmatrix} J' & 1 & J \\ -K' & q & K \end{pmatrix}^2 |\tilde{B}_q^1|^2 + \frac{2}{35}\begin{pmatrix} J' & 3 & J \\ -K' & r & K \end{pmatrix}^2 |\tilde{B}_r^3|^2\right\}, \tag{10a}$$

$$S_h(JK, J'K') = (2J+1)(2J'+1)\left\{\frac{1}{45}\begin{pmatrix} J' & 1 & J \\ -K' & q & K \end{pmatrix}^2 |\tilde{B}_q^1|^2 + \frac{4}{105}\begin{pmatrix} J' & 3 & J \\ -K' & r & K \end{pmatrix}^2 |\tilde{B}_r^3|^2\right\}. \tag{10b}$$

The values of the squared 3-j coefficients remain unaffected by an interchange of two columns or a change in signs of the elements in the lower row. Since, moreover, one has the relation $|\tilde{B}_m^l|^2 = |\tilde{B}_{-m}^l|^2$ for the molecular parameters, it results from Eqs (10) that the strengths of the transitions $S_k(JK, J'K')$ and $S_k(J'K', JK)$ are equal to each other.

The vertical and horizontal scattered components (1) have the intensities:

$$V_v^{2\omega+\omega_{R'R}} = \frac{2\pi}{c^5}(2\omega+\omega_{R'R})^4 I_0^2 g_{I,K} \frac{N_{JK}}{2J+1} S_v(JK, J'K'), \tag{11a}$$

$$H_v^{2\omega+\omega_{R'R}} = \frac{2\pi}{c^5}(2\omega+\omega_{R'R})^4 I_0^2 g_{I,K} \frac{N_{JK}}{2J+1} S_h(JK, J'K'), \tag{11b}$$

where

$$\omega_{R'R} = \frac{1}{\hbar}\{E(J, K) - E(J', K')\}. \tag{12}$$

At linear scattering, the intensity of the line for the transition $JK \rightarrow J'K'$ depends (for any ΔJ and well-defined ΔK) only on one element, $\tilde{B}_q^2$, of the molecule's polarizability tensor [16, 21]. In the present case, we deal with a dependence on two elements: $\tilde{B}_q^1$ and $\tilde{B}_r^3$. This is due to the circumstance that the anisotropic part of two-photon scattering is described by a spherical tensor of a single (the second) rank, whereas in three-photon scattering we have tensors of two (the first and third) ranks.

The molecular symmetry decides which of the parameters $|\tilde{B}_m^l|^2$ will differ from zero. For molecules having a centre of symmetry all parameters vanish. For noncentrosymmetric linear as well as symmetric top molecules, we give in Appendix A the relation between $|\tilde{B}_m^l|^2$ and the hyperpolarizability tensor elements in a Cartesian co-ordinate system the 3-axis of which is the symmetry axis of the molecule. The properties of the Wigner coefficients occurring in Eqs (9) and (10) lead to the selection rules $\Delta J = 0, \pm 1, \pm 2, \pm 3$; however, if $K = 0$ and $K' = 0$ simultaneously, then only transitions with $\Delta J = \pm 1, \pm 3$, are permitted [11]. The selection rules for the quantum numbers K depend on which of the elements $|\tilde{B}_m^l|^2$ are non-zero for a given symmetry, because the relation $\Delta K = m$ has to be fulfilled.

It is noteworthy that in three-photon scattering no isotropic component, independent of molecular orientation in space, related with a spherical tensor of rank zero, occurs. A Q-branch appears only if the selection rules $\Delta J = 0$, $\Delta K = 0$ are permitted, in the part described by spherical tensors of ranks 1 and 3.

Defining the depolarization ratio of the spectral line of scattered light as:

$$D_v^{2\omega + \omega_{n'n}} = \frac{H_v^{2\omega + \omega_{n'n}}}{V_v^{2\omega + \omega_{n'n}}} \tag{13}$$

and using Eq. (11), we obtain:

$$D_v^{2\omega + \omega_{R'R}} = \frac{\dfrac{1}{45} \begin{pmatrix} J' & 1 & J \\ -K' & q & K \end{pmatrix}^2 |\tilde{B}_q^1|^2 + \dfrac{4}{105} \begin{pmatrix} J' & 3 & J \\ -K' & r & K \end{pmatrix}^2 |\tilde{B}_r^3|^2}{\dfrac{1}{5} \begin{pmatrix} J' & 1 & J \\ -K' & q & K \end{pmatrix}^2 |\tilde{B}_q^1|^2 + \dfrac{2}{35} \begin{pmatrix} J' & 3 & J \\ -K' & r & K \end{pmatrix}^2 |\tilde{B}_r^3|^2} . \tag{14}$$

The depolarization ratio of each of the rotational lines of linear scattering is equal to 3/4 [21]. In our case, owing to the presence of two parameters, the ratio (14) is in general a function of J and K. For all lines of the branches O, S, N, T as well as for those with $\Delta K = \pm 2, \pm 3$ in the branches P and R, the Wigner coefficients at the parameter $|\tilde{B}_q^1|^2$ vanish and their depolarization ratio (14) amounts to 2/3. From the form of the non-vanishing parameters $|\tilde{B}_m^l|^2$ listed in Appendix A, the spectrum of molecules having the symmetries D_{3h}, D_3 and C_{3h} contain only lines with $\Delta K = \pm 3$ whereas, for the symmetries S_4, T_d, T and D_{2d} — lines with $\Delta K = \pm 2$ only. Hence, for the above symmetries the depolarization ratio (14) of each of the rotational lines, present in the spectrum, amounts to 2/3. Moreover, the equality of transition strengths for $JK \rightarrow J'K'$ and $J'K' \rightarrow JK$ leads to the conclusion that Stokes and anti-Stokes lines, disposed symmetrically about the centre of the spectrum, have the same depolarization ratio.

Summation of the intensities of all the permitted rotational lines yields an expression for the total intensity of the hyper-Rayleigh line:

$$V_v^{2\omega} = \frac{\pi}{70c^5} (2\omega)^4 I_0^2 N \left\{ 7 \sum_q |\tilde{B}_q^1|^2 + 2 \sum_r |\tilde{B}_r^3|^2 \right\}. \tag{15}$$

$H_v^{2\omega}$ is obtained by multiplying the first term of the sum by 1/9 and the second term by 2/3. These formulas are in agreement with the results of Kielich [3], derived by classical averaging over all possible orientations of the molecule.

3. Numerical calculations for selected axially-symmetric molecules

In order that our numerical calculations shall not involve the intensity and frequency of incident light, we introduce the following factor of rotational structure:

$$F_v(J, K, J', K') = \exp\left\{ -\frac{E(J, K)}{kT} \right\} \frac{g_{I,K}}{35Z} (2J+1)(2J'+1)$$

$$\times \left\{ 7 \begin{pmatrix} J' & 1 & J \\ -K' & q & K \end{pmatrix}^2 |\tilde{B}_q^1|^2 + 2 \begin{pmatrix} J' & 3 & J \\ -K' & r & K \end{pmatrix}^2 |\tilde{B}_r^3|^2 \right\}, \tag{16}$$

where Z is the rotational partition function. Since for linear molecules $K \equiv 0$, the factor $F_v(J, J')$ assumes the form (with $hB \ll kT$):

$$F_v(J, J') = \frac{1}{35} \frac{hB}{kT} \exp\left[-\frac{hBJ(J+1)}{kT} \right] (2J+1)(2J'+1) \left\{ 7 \begin{pmatrix} J' & 1 & J \\ 0 & 0 & 0 \end{pmatrix}^2 |\tilde{B}_0^1|^2 \right.$$

$$\left. + 2 \begin{pmatrix} J' & 3 & J \\ 0 & 0 & 0 \end{pmatrix}^2 |\tilde{B}_0^3|^2 \right\}, \tag{17}$$

whereas for C_{3v} symmetry:

$$F_v(J, K, J', K') = \frac{g_{I,K}}{35(4I^2+4I+1)} \sqrt{\frac{B^2Ah^3}{\pi(kT)^3}} \exp\left\{ -\frac{[BJ(J+1)+(A-B)K^2]h}{kT} \right\}$$

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

$$\left. + 2 \begin{pmatrix} J' & 3 & J \\ -K' & 3 & K \end{pmatrix}^2 |\tilde{B}_3^3|^2 + 2 \begin{pmatrix} J' & 3 & J \\ -K' & -3 & K \end{pmatrix}^2 |\tilde{B}_{-3}^3|^2 \right\}, \tag{18}$$

A and B denoting rotational constants of the molecules, and I — the value of the nuclear spin of the molecule. With available values of hyperpolarizability tensor elements $\tilde{b}_{\alpha\beta\gamma}^{2\omega}$ and rotational constants, we calculated the functions $F_v(J, K, J', K')$ for the linear molecules CO, NO, HF ($C_{\infty v}$) and the molecule NH_3 (C_{3v}). The numerical values assumed in our calculations are given in Table I.

Since the spectra under consideration present several branches, we refrain from adducing graphs of the factor $F_v(J, K, J', K')$ for each branch separately. Instead, we plot the resultant spectral distribution $F_v(\Delta\tilde{v}_R)$, involving sums of factors $F_v(J, K, J', K')$

TABLE I

Values of hyperpolarizability tensor elements and rotational constants assumed in the present calculations

Molecule	$b^{2\omega}_{333}$ $\times 10^{32}$ cm^5/esu	$b^{2\omega}_{113}$ $\times 10^{32}$ cm^5/esu	$b^{2\omega}_{111}$ $\times 10^{32}$ cm^5/esu	$\tilde{A}$ [18] cm^{-1}	$\tilde{B}$ [18] cm^{-1}	No of the graph of function $F_v(\Delta v_R)$
CO	−98.28	−15.16 [22]			1.931	1
CO	19.73	−17.10 [23]			1.931	2
NO	22.39	−3.232 [23]			1.705	3
HF	−23.30	5.199 [23]			20.939	4
NH₃	−13.18	−2.646	−1.323 [23]	6.30	9.94	5
NH₃	−2.690	−5.469	7.624 [24]	6.30	9.94	6

from branches with the same frequency displacement $\Delta\tilde{v}_R$ as compared with the pure hyper-Rayleigh line with frequency exactly equal to $2\tilde{v}$.

A comparison of the graphs (1–6) shows that the shape of the spectrum is strongly influenced by the sign and value of the hyperpolarizability tensor elements. If one of the parameters $|\tilde{B}^l_m|^2$ predominates, as it is the case of CO from the data of O'Hare [22] and
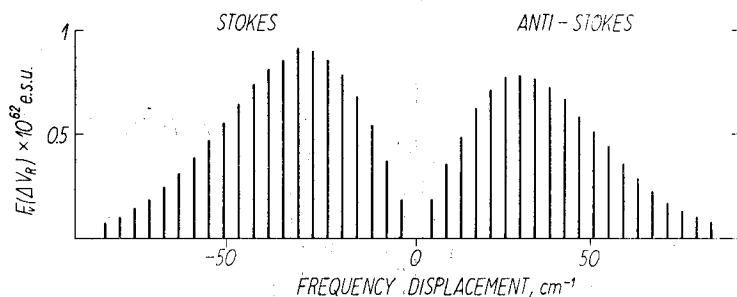

Fig. 1. Graph of $F(\Delta v_R)$ plotted with O'Hare's [22] values of hyperpolarizability tensor elements, for the molecule CO

of NH₃ from those of Hush [23], the branch associated with that parameter is decisive in defining the shape (Figs 1 and 5). If several parameters $|\tilde{B}^l_m|^2$ are of the same order of magnitude, the shape of the spectrum becomes complicated (Figs 2, 3, 4, 6). The feasibility of comparisons between the experimentally recorded and theoretically predicted shape will permit rapid assessments of the correctness of quantum-mechanically calculated hyperpolarizability tensor elements [22–24].
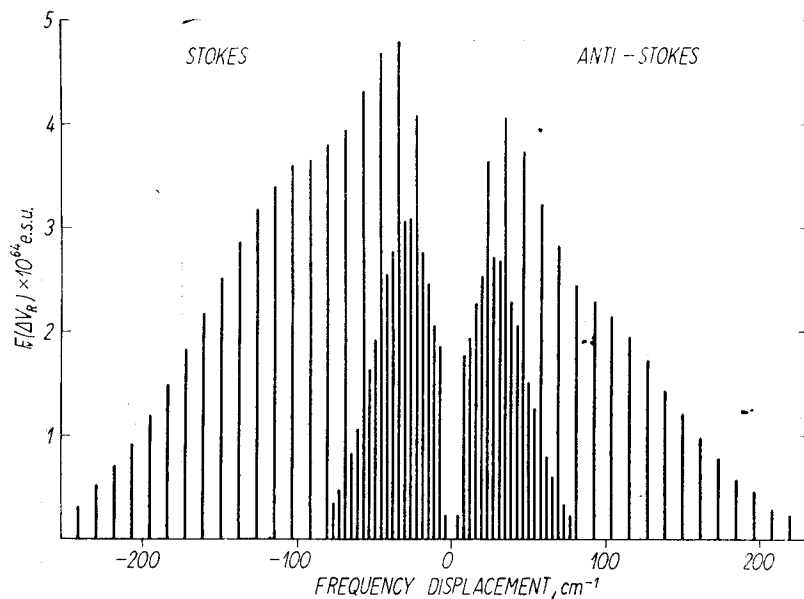
Fig. 2. Graph of $F(\Delta\nu_R)$ plotted with Hush's [23] values of hyperpolarizability tensor elements, for the molecule CO
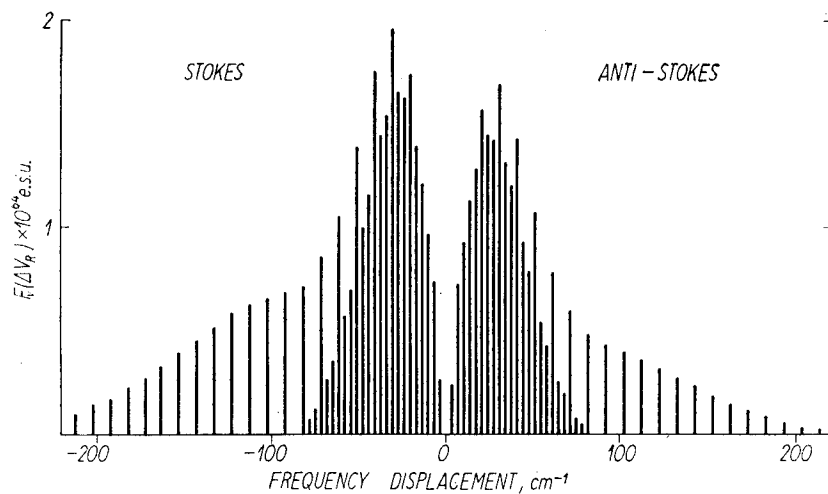

Fig. 3. Graph of $F(\Delta\nu_R)$ plotted with Hush's [23] values of hyperpolarizability tensor elements, for the molecule NO
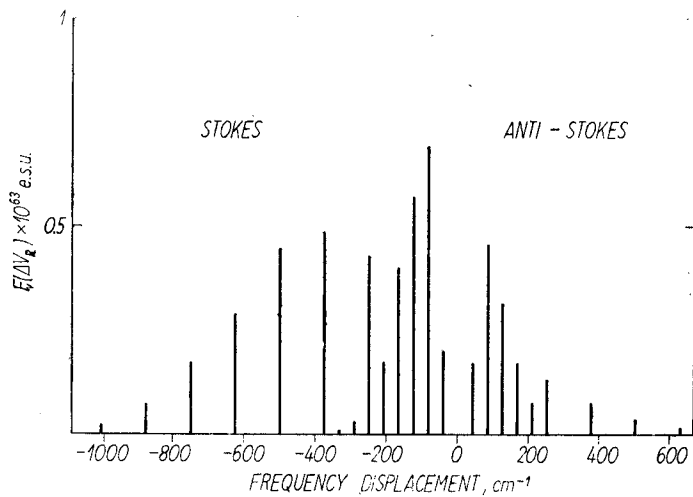
Fig. 4. Graph of $F(\Delta\nu_R)$ plotted with Hush's [23] values of hyperpolarizability tensor elements, for the molecule HF
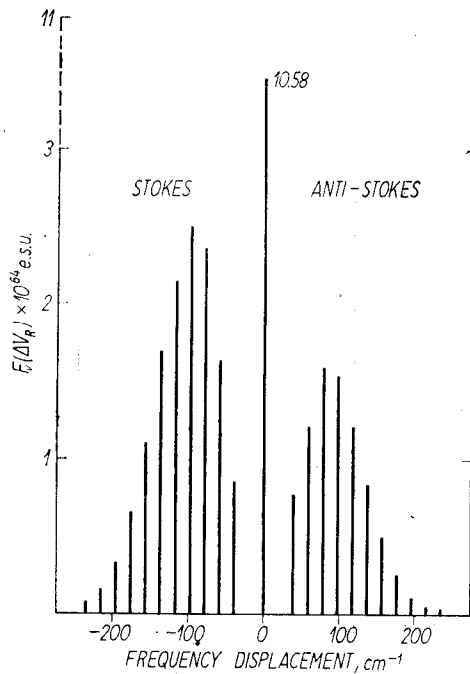

Fig. 5. Graph of $F(\Delta\nu_R)$ plotted with Hush's [23] values of hyperpolarizability tensor elements, for the molecule NH_3
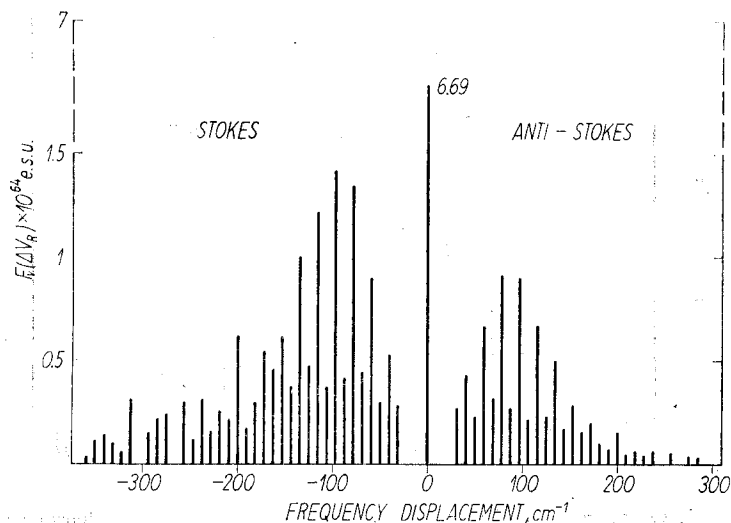
Fig. 6. Graph of $F(\Delta\nu_R)$ plotted with Moccia's [24] values of hyperpolarizability tensor elements, for the molecule NH_3

Our evaluations led to scattered intensities for CO, NO, HF and NH_3 that are larger than for methane, which was studied by Maker [10]. Hence, those molecules present more advantageous conditions for rotation-structural observations of hyper-Rayleigh spectra.

The authors wish to thank the Physics Committee of the III Department of the Polish Academy of Sciences for sponsoring this investigation.

APPENDIX A

Non-zero parameters $|\tilde{B}_m^i|^2$ for various molecular symmetries

Point groups	$|\tilde{B}_m^l|^2$
D_3 and D_{3h}	$|\tilde{B}_3^3|^2 = |\tilde{B}_{-3}^3|^2 = 2(b_{111}^{2\omega})$
C_{3h}	$|\tilde{B}_3^3|^2 = |\tilde{B}_{-3}^3|^2 = 2[(b_{111}^{2\omega})^2 + (b_{222}^{2\omega})^2]$
C_{3v}	$|\tilde{B}_0^1|^2 = \frac{3}{5}(b_{333}^{2\omega} + 2b_{113}^{2\omega})^2$
	$|\tilde{B}_0^3|^2 = \frac{2}{5}(b_{333}^{2\omega} - 3b_{113}^{2\omega})^2$
	$|\tilde{B}_3^3|^2 = |\tilde{B}_{-3}^3|^2 = 2(b_{111}^{2\omega})^2$
C_3	$|\tilde{B}_0^1|^2 = \frac{3}{5}(b_{333}^{2\omega} + 2b_{113}^{2\omega})^2$
	$|\tilde{B}_0^3|^2 = \frac{2}{5}(b_{333}^{2\omega} - 3b_{113}^{2\omega})^2$
	$|\tilde{B}_3^3|^2 = |\tilde{B}_{-3}^3|^2 = 2[(b_{111}^{2\omega})^2 + (b_{222}^{2\omega})^2]$

Point groups	$\lvert \tilde{B}_m^l \rvert^2$
$C_4 \ldots C_\infty$ and $C_{4v} \ldots C_{\infty v}$	$\lvert \tilde{B}_0^1 \rvert^2 = \tfrac{3}{5}(b_{333}^{2\omega} + 2b_{113}^{2\omega})^2$
	$\lvert \tilde{B}_0^3 \rvert^2 = \tfrac{2}{5}(b_{333}^{2\omega} - 3b_{113}^{2\omega})^2$
S_4	$\lvert \tilde{B}_2^3 \rvert^2 = \lvert \tilde{B}_{-2}^3 \rvert^2 = 3[(b_{113}^{2\omega})^2 + (b_{123}^{2\omega})^2]$
$D_{2d} \quad T, \ T_d$	$\lvert \tilde{B}_2^3 \rvert^2 = \lvert \tilde{B}_{-2}^3 \rvert^2 = 3(b_{123}^{2\omega})^2$

APPENDIX B

Expressions for the squared 3-j Wigner coefficients

The symbol $a^{(b)}$ has the following meaning:

$$a^{(b)} \equiv a(a-1) \ldots (a-b+1).$$

$$\begin{pmatrix} J & 1 & J \\ -K & 0 & K \end{pmatrix}^2 = \frac{4K^2}{(2J+2)^{(3)}},$$

$$\begin{pmatrix} J+1 & 1 & J \\ -K & 0 & K \end{pmatrix}^2 = \frac{2[(J+1)^2 - K^2]}{(2J+3)^{(3)}},$$

$$\begin{pmatrix} J & 3 & J \\ -K & 0 & K \end{pmatrix}^2 = \frac{16K^2(3J^2 + 3J - 5K - 1)^2}{(2J+4)^{(7)}},$$

$$\begin{pmatrix} J & 3 & J \\ -K-3 & 3 & K \end{pmatrix}^2 = \frac{20(J+K+3)^{(3)}(J-K)^{(3)}}{(2J+4)^{(7)}},$$

$$\begin{pmatrix} J & 3 & J \\ -K-2 & 2 & K \end{pmatrix}^2 = \frac{120(K+1)^2(J+K+2)^{(2)}(J-K)^{(2)}}{(2J+4)^{(7)}},$$

$$\begin{pmatrix} J+1 & 3 & J \\ -K & 0 & K \end{pmatrix}^2 = \frac{12[(J+1)^2 - K^2][(J+K)^{(2)} + (J-K)^{(2)} - 3(J^2 - K^2)]^2}{(2J+5)^{(7)}},$$

$$\begin{pmatrix} J+1 & 3 & J \\ -K-2 & 2 & K \end{pmatrix}^2 = \frac{10(J-3K-2)^2(J-K)(J+K+3)^{(3)}}{(2J+5)^{(7)}},$$

$$\begin{pmatrix} J+1 & 3 & J \\ -K-3 & 3 & K \end{pmatrix}^2 = \frac{15(J+K+4)^{(4)}(J-K)^{(2)}}{(2J+5)^{(7)}},$$

$$\begin{pmatrix} J+2 & 3 & J \\ -K & 0 & K \end{pmatrix}^2 = \frac{120K^2(J+K+2)^{(2)}(J-K+2)^{(2)}}{(2J+6)^{(7)}},$$

$$\begin{pmatrix} J+2 & 3 & J \\ -K-2 & 2 & K \end{pmatrix}^2 = \frac{4(2J-3K)^2(J+K+4)^{(4)}}{(2J+6)^{(7)}},$$

$$\begin{pmatrix} J+2 & 3 & J \\ -K-3 & 3 & K \end{pmatrix}^2 = \frac{6(J-K)\,(J+K+5)^{(5)}}{(2J+1)^{(7)}},$$

$$\begin{pmatrix} J+3 & 3 & J \\ -K & 0 & K \end{pmatrix}^2 = \frac{20(J+K+3)^{(3)}(J-K+3)^{(3)}}{(2J+7)^{(7)}},$$

$$\begin{pmatrix} J+3 & 3 & J \\ -K-2 & 2 & K \end{pmatrix}^2 = \frac{6(J-K+1)\,(J+K+5)^{(5)}}{(2J+7)^{(7)}},$$

$$\begin{pmatrix} J+3 & 3 & J \\ -K-3 & 3 & K \end{pmatrix}^2 = \frac{(J+K+6)^{(6)}}{(2J+7)^{(7)}}.$$

REFERENCES

[1] S. Kielich, *Opto-electron.* **2**, 125 (1970); *Ferroelectrics* **4**, 257 (1972).

[2] R. W. Terhune, P. D. Maker, C. M. Savage, *Phys. Rev. Lett.* **14**, 681 (1965).

[3] S. Kielich, *Bull. Acad. Pol. Sci. Sér. Sci. Math. Astron. Phys.* **12**, 53 (1964); *Physica* **30**, 1717 (1964); *Acta Phys. Pol.* **26.**, 135 (1964).

[4] Y. Y. Li, *Acta Phys. Sinica* **20**, 164 (1964).

[5] S. J. Cyvin, J. E. Rauch, J. C. Decius, *J. Chem. Phys.* **43**, 4083 (1965).

[6] D. A. Long, L. Stanton, *Proc. Roy. Soc. (London)* **A318**, 441 (1970); D. A. Long in *Essays in Structural Chemistry*, ed. D. ·A. Long, A. J. Downs, L. A. K. Stavley (Macmillan), 1971, Chap. 2.

[7] J. F. Verdieck, S. H. Peterson, M. Savage, P. D. Maker, *Chem. Phys. Lett.* **7**, 219 (1970).

[8] S. Kielich, J. R. Lalanne, F. B. Martin, *J. Raman Spectrosc.* **1**, 119 (1973).

[9] P. D. Maker, *Phys. Rev.* **1**, 923 (1970).

[10] P. D. Maker in: *Physics of Quantum Electronics*, Mc Graw-Hill, New York 1966, pp. 60–66.

[11] T. Bancewicz, Z. Ożgo, S. Kielich, *J. Raman Spectrosc.* **1**, 177 (1973).

[12] S. Kielich, T. Bancewicz, Z. Ożgo, *II. Internationale Tagung Laser und ihre Anwendungen*, Dresden 1973.

[13] T. Bancewicz, Z. Ożgo, S. Kielich, *Phys. Lett.* **44A**, 407 (1973).

[14] S. Kielich, Z. Ożgo, *Optics Communications* **8**, 417 (1973).

[15] A. P. Jucis, A. A. Bandzaitis, *Teoria Momenta Kolichestva Dvizhenia v Kvantovoy Mekhanike*, Vilnius 1965.

[16] K. Altman, G. Strey, *J. Mol. Spectrosc.* **44**, 571 (1972).

[17] Ying-Nan Chiu, *J. Chem. Phys.* **52**, 4950 (1970).

[18] G. Herzberg, *Molecular Spectra and Molecular Structure*, Vols I and II, Van Nostrand Reinhold, New York 1950.

[19] E. B. Wilson, J. C. Decius, P. C. Cross, *Molecular Vibrations*, Mc Graw-Hill, New York 1955.

[20] B. Berestetskii, Y. M. Lifshits, L. P. Pitayevskii, *Relativisticheskaya Kvantovaya Teoria*, Nauka 1968, Part I., A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, Princeton, New Jersey 1957.

[21] G. Placzek, E. Teller, *Z. Phys.* **81**, 209 (1933).

[22] J. M. O'Hare, R. P. Hurst, *J. Chem. Phys.* **46**, 2356 (1967).

[23] N. S. Hush, M. L. Williams, *Theor. Chim. Acta* **25**, 346 (1972).

[24] G. P. Arrighini, M. Maestro, R. Moccia, *Symposium of the Faraday Society* 1968, No. 2, p. 48.