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THE QUANTUM MECHANICS OF ROTATING AND TRANSLATING MOLECULES: RAMAN SCATTERING

M.W. EVANS[1]

Dept. of Chemistry, Bourne Laboratory, Royal Holloway and Bedford New College, University of London, Egham Hill, Egham, Surrey TW20 0EW, UK

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Group theory is used to investigate the selection rules and quantum line intensity of Raman scattering from a molecule that is simultaneously a harmonic oscillator and a rigid rotor. The rigid rotor Raman scattering selection rules are modified to

$$\Delta J = 0, \pm 2, \pm 4 \quad (n \text{ odd}), \qquad \Delta J = 0, \pm 2, \quad \Delta n = 0 \quad (n \text{ even}), \qquad \Delta J = \pm 3, \Delta n = 1,$$

where n is the quantum number of the linear harmonic oscillator. The latter's selection rules are modified from $\Delta n = \pm 1$ to $\Delta n = 0, \pm 1$. The intensity distribution of the envelopes of the first few rototranslational Raman lines are established as the appropriate number of totally symmetric representations in each transition matrix. The theory is checked against what little data are available, specifically on lattice isolated HD, and found to be in close agreement with observed transitions in this case.

1. Introduction

The quantised rotation and translation of small molecules [1, 2] under controlled conditions, using matrix isolation, are no longer mutually independent [3–8]. Evidence for this is available from the experimental work of Ewing [9], and the theoretical analysis of Friedman and Kimel [10–13]. These authors looked at an example of rotation translation coupling involving a simple diatomic, hydrogen deuteride, HD, whose motion is clearly quantised. The rototranslational spectrum was found to be radically different from either a pure rotational spectrum, or a rattling mode spectrum describable with the simple harmonic oscillator. $\Delta J = 0, 1, 2$, and 3 absorptions were observable in the far infrared from the simultaneously rotating and translating HD molecule trapped in a rare gas crystal.

The analysis of mutually influential rotation and translation is clearly a useful complement to conventional infrared and Raman spectroscopy, but the spectral analysis depends on having available a relatively simple and straightforward method of obtaining selection rules and intensity distributions both in the infrared and Raman. This short communication is intended as a guide to analysis of such data as they become available for molecules of various point group symmetries trapped in a matrix isolated condition and simultaneously rotating and oscillating within the matrix cavity. This not only emphasises the interdependence of quantised rotation and oscillation in the matrix trapped molecule, but anticipates the availability of suitable infrared and Raman data with which to explore these complicated and revealing phenomena. The method is illustrated with reference to Raman scattering from a molecule whose wave functions are derived from the harmonic oscillator and rigid rotor. For the oscillator quantum number n the new Raman selection rules are derived for $\Delta n = 0$ and $\Delta n = 1$ from the Clebsch–Gordan theorem [3–5], and estimates of relative intensities are made using group theory.

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[1] Also at Dept. of Physics, University of Lancaster, LA1 4YB, UK and I.B.M., Dept. 48B/428, Kingston, NY 12401, USA.

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2. Theory

The solution of Schrödinger's equation [3–8] for a rigid molecule, that is simultaneously a rigid rotor and a harmonic oscillator, is found from the assumption that the wave function of the combined motions is a simple product of those of pure rotation and pure harmonic oscillation,

$$\Psi_{tr} = \Psi_t \Psi_r , \tag{1}$$

in analogy with the Van Vleck theory of vibronic coupling [3–8]. If a transition between two roto-translational eigenstates $\Psi_{tr}^{(1)}$ and $\Psi_{tr}^{(2)}$, connected by an operator $\hat{P}$, is to have finite probability, at least one matrix element of the type,

$$\langle \Psi_t^{(1)} \Psi_r^{(1)} | \hat{P} | \Psi_t^{(2)} \Psi_r^{(2)} \rangle \tag{2}$$

must differ from zero.

For infrared absorption, $\hat{P}$ is the transition dipole moment, whose symmetry is $\mathrm{D}_\mathrm{u}^{(1)}$. For Raman scattering $\hat{P}$ is the polarisability tensor $\boldsymbol{\alpha}$, whose symmetry is $\mathrm{D}_\mathrm{g}^{(0)} + \mathrm{D}_\mathrm{g}^{(2)}$, where the D-representations are irreducible representations of the $\mathrm{R}_\mathrm{h}(3)$ rotation reflection point group [3–8]. Matrix elements of (2) exist in group theory if the product of symmetry representations

$$\Gamma(\Psi_t^{(1)}) \Gamma(\Psi_r^{(1)}) \Gamma(\hat{P}) \Gamma(\Psi_t^{(2)}) \Gamma(\Psi_r^{(2)}) \tag{3}$$

contains at least once the totally symmetric irreducible representation, $\mathrm{D}_\mathrm{g}^{(0)}$.

We obtain the selection rules by a consideration of the Clebsch–Gordan theorem [3–8] for the transition between two wavefunctions of type (1) via the operator $\hat{P}$.

For the case $\Delta n = 0$, n even, the symmetry of Ψ_{tr} is

$$\Gamma(\Psi_{tr}) = \Psi_t \Psi_r = \mathrm{D}_\mathrm{g}^{(0)} \mathrm{D}^{(J)} = \mathrm{D}^{(J)} , \tag{4}$$

where J is the rotational quantum number. This result is obtained from the symmetry $\mathrm{D}_\mathrm{g}^{(0)}$ of the translational harmonic oscillator Ψ_t for all even n. For a transition of the type $\Delta n = 0$, n even, to be allowed in Raman scattering, the product

$$\mathrm{D}_\mathrm{g}^{(0)} \mathrm{D}^{(J)} \mathrm{D}_\mathrm{g}^{(0)} \mathrm{D}^{(J')} = \mathrm{D}^J \mathrm{D}^{J'} \tag{5}$$

must contain the symmetry $\mathrm{D}_\mathrm{g}^{(2)}$ of the polarisability operator $\boldsymbol{\alpha}$. The Clebsch–Gordan theorem gives

$$\mathrm{D}^{(J)} \mathrm{D}^{(J')} = \mathrm{D}^{(J+J')} + \cdots + \mathrm{D}^{|J-J'|} \tag{6}$$

and the right hand side can contain $\mathrm{D}_\mathrm{g}^{(2)}$ if and only if (1) both $\mathrm{D}^{(J)}$ and $\mathrm{D}^{(J')}$ are gerade or both are ungerade; (2) $\Delta J = 0, \pm 2$.

The combined selection rule is therefore

$$\Delta n = 0, \; n \text{ even} , \quad \Delta J = 0, \pm 2 . \tag{7}$$

For the case $\Delta n = 0$, n odd the symmetry of Ψ_{tr} is

$$\Gamma(\Psi_{tr}) = \mathrm{D}_\mathrm{u}^{(1)} \mathrm{D}^{(J)} = \mathrm{D}^{(J+1)} + \mathrm{D}^{(J)} + \mathrm{D}^{(J-1)} , \tag{8}$$

because Ψ_t for the harmonic oscillator is $\mathrm{D}_\mathrm{u}^{(1)}$ for all odd n. Thus harmonic oscillation for odd n, splits the rotational symmetry $\mathrm{D}^{(J)}$ into a sum of three parts, the right hand side of the symmetry representation (8). The selection rules in this case are therefore derived from the Clebsch–Gordan expansion

$$(\mathrm{D}^{(J+1)} + \mathrm{D}^{(J)} + \mathrm{D}^{(J-1)}) \times (\mathrm{D}^{(J'+1)} + \mathrm{D}^{(J')} + \mathrm{D}^{(J'-1)}) , \tag{9}$$

which contains $\mathrm{D}_\mathrm{g}^{(2)}$ if and only if (1) both $\mathrm{D}^{(J)}$ and $\mathrm{D}^{(J')}$ are gerade or both are ungerade; (2) $\Delta J = 0, \pm 2, \pm 4$.

The full selection rule is therefore:

$$\Delta n = 0, \quad n \text{ odd} , \quad \Delta J = 0, \pm 2, \pm 4 .$$

This rule clearly allows the transition $\Delta J = \pm 4$ for $\Delta n = 0$, odd n.

For the case $\Delta n = 1$, all n, the selection rule $\Delta n = \pm 1$ implies the transition from an ungerade to gerade harmonic oscillator energy level, accompanied by simultaneous ΔJ transitions. The $\Delta n = 1$ transition can correspond to n even → n

Table I
Symmetry of polarisability, translational and rotational wave functions

Point group	$\Gamma(\alpha)$	$\Gamma(\Psi_t^{2m})$	$\Gamma(\Psi_t^{(2m+1)})$	$\Gamma(\Psi_r)$ $J=0$	$\Gamma(\Psi_r)$ $J=1$	$\Gamma(\Psi_r)$ $J=2$	$\Gamma(\Psi_r)$ $J=3$
C_1	$9A$	A	$3A$	A	$3A$	$5A$	$7A$
C_2	$5A+4B$	A	$A+2B$	A	$A+2B$	$3A+2B$	$3A+4B$
C_{1h}	$5A'+4A''$	A'	$2A'+A''$	A''	$A'+2A''$	$2A'+3A''$	$3A'+4A''$
C_{2h}	$5A_g+4B_g$	A_g	A_u+2B_u	A_u	A_g+2B_g	$3A_u+2B_u$	$3A_g+4B_g$
C_{2v}	$3A_1+2A_2+2B_1+2B_2$	A_1	$A_1+B_1+B_2$	A_2	$A_2+B_1+B_2$	$A_1+2A_2+B_1+B_2$	$A_1+2A_2+2B_1+2B_2$
C_{3v}	$2A_1+3E$	A_1	A_1+E	A_2	A_2+E	A_2+2E	A_1+2A_2+2E
$C_{\infty v}$	$2\Sigma^++2\Pi+\Delta$	Σ^+	$\Sigma^++\Pi$	Σ^-	$\Sigma^-+\Pi$	$\Sigma^-+\Pi+\Delta$	$\Sigma^-+\Pi+\Delta+\Phi$
D_{2h}	$3A_g+2B_{1g}+2B_{2g}+2B_{3g}$	A_g	$B_{1u}+B_{2u}+B_{3u}$	A_u	$B_{1g}+B_{2g}+B_{3g}$	$2A_u+B_{1u}+B_{2u}+B_{3u}$	$A_g+2B_{1g}+2B_{2g}+2B_{3g}$
D_{3h}	$2A_1'+E'+2E''$	A_1'	$A_2''+E'$	A_1''	$A_2'+E''$	$A_1''+E''+E'$	$A_1''+A_2'+A_2''+E'+E''$
D_{6h}	$2A_{1g}+2E_{1g}+E_{2g}$	A_{1g}	$A_{2u}+E_{1u}$	A_{1u}	$A_{2g}+E_{1g}$	$A_{1u}+E_{1u}+E_{2u}$	$A_{2g}+B_{1g}+B_{2g}+E_{1g}+E_{2g}$
$D_{\infty h}$	$2\Sigma_g^++2\Pi_g+\Delta_g$	Σ_g^+	$\Sigma_u^++\Pi_u$	Σ_u^-	$\Sigma_g^-+\Pi_g$	$\Sigma_u^-+\Pi_u+\Delta_u$	$\Sigma_g^-+\Pi_g+\Delta_g+\Phi_g$
T_d	A_1+E+T_2	A_1	T_2	A_2	T_1	$E+T_1$	$A_2+T_1+T_2$
O_h	$A_{1g}+E_g+T_{2g}$	A_{1g}	T_{1u}	A_{1u}	T_{1g}	E_u+T_{2u}	$A_{2g}+T_{1g}+T_{2g}$

Table II
Symmetries of some roto-translational wave functions

Point group	$\Gamma(\Psi_t^{2m+1}\Psi_r^{J=0})$	$\Gamma(\Psi_t^{2m+1}\Psi_r^{J=1})$	$\Gamma(\Psi_t^{2m+1}\Psi_r^{J=2})$	$\Gamma(\Psi_t^{2m+1}\Psi_r^{J=3})$
C_1	$3A$	$9A$	$15A$	$21A$
C_2	$A+2B$	$5A+4B$	$7A+8B$	$11A+10B$
C_{1h}	$2A''+A'$	$4A'+5A''$	$7A'+8A''$	$10A'+11A''$
C_{2h}	A_g+2B_g	$5A_u+4B_u$	$7A_g+8B_g$	$11A_u+10B_u$
C_{2v}	$A_2+B_1+B_2$	$2A_1+3A_2+2B_1+2B_2$	$3A_1+4A_2+4B_1+4B_2$	$5A_1+6A_2+5B_1+5B_2$
C_{3v}	A_2+E	A_1+2A_2+3E	$2A_1+3A_2+5E$	$3A_1+4A_2+7E$
$C_{\infty v}$	$\Sigma^-+\Pi$	$2\Sigma^-+\Sigma^++2\Pi+\Delta$	$\Sigma^++2\Sigma^-+3\Pi+2\Delta+\Phi$	$\Sigma^++2\Sigma^-+3\Pi+3\Delta+2\Phi+\Gamma$
D_{2h}	$B_{1g}+B_{2g}+B_{3g}$	$3A_u+2B_{1u}+2B_{2u}+2B_{3u}$	$3A_g+4B_{1g}+4B_{2g}+4B_{3g}$	$6A_g+5B_{1g}+5B_{2g}+5B_{3g}$
D_{3h}	$A_2'+E''$	$2A_1''+A_2''+2E'+E''$	$A_1'+2A_2'+A_1''+A_2''+2E'+3E''$	$2A_1'+2A_2'+2A_1''+A_2''+3E'+4E''$
D_{6h}	$A_{2g}+E_{1g}$	$2A_{1u}+A_{2u}+3E_{2u}$	$A_{1g}+2A_{2g}+B_{1g}+B_{2g}+3E_{1g}+2E_{2g}$	$2A_{1u}+A_{2u}+2B_{1u}+2B_{2u}+3E_{1u}+4E_{2u}$
$D_{\infty h}$	$\Sigma_g^-+\Pi_g$	$\Sigma_u^++2\Sigma_u^-+2\Pi_u+\Delta_u$	$\Sigma_g^++2\Sigma_g^-+3\Pi_g+2\Delta_g+\Phi_g$	$\Sigma_u^++2\Sigma_u^-+3\Pi_u+3\Delta_u+2\Phi_u+\Gamma_u$
T_d	T_1	$A_2+E+T_1+T_2$	$A_2+E+2T_1+2T_2$	$A_1+A_2+2E+3T_1+2T_2$
O_h	T_{1g}	$A_{1u}+E_u+T_{1u}+T_{2u}$	$A_{2g}+E_g+2T_{1g}+2T_{2g}$	$A_{1u}+A_{2u}+2E_u+3T_{1u}+2T_{2u}$

odd or alternatively n odd → n even. In the first case the appropriate Clebsch–Gordan expansion of

$$D_g^{(0)}D^{(J)}D_u^{(1)}D^{(J')} \tag{10}$$

must contain $D_g^{(2)}$ for a Raman transition to be observed, and in the second case

$$D_u^{(1)}D^{(J)}D_g^{(0)}D^{(J')} . \tag{11}$$

In both cases this is possible only if $\Delta J = \pm 3$, so that the full selection rule is

$$\Delta n = 1, \quad \text{all } n\,, \quad \Delta J = \pm 3\,.$$

These rules introduce the transitions $\Delta J = \pm 3$ and $\Delta J = \pm 4$ which enrich the rototranslational spectrum and are not allowed when rotation translation coupling is absent. They should, however, be observable in the spectra of lattice trapped small molecules such as HD, H_2, D_2, H_2O, and so on.

3. Occurrences of the totally symmetric representation in product (3): relative intensities of Raman transitions.

For the various molecular point groups the number of occurrences in product (3) of the group's totally symmetric representation indicates the relative expected intensities in (2) of transitions allowed by the selection rules. In order to calculate this number for each point group it is necessary to know $\boldsymbol{\Gamma}(\boldsymbol{\alpha})$ within that molecular point group. This is given in table I for several point groups of interest.

The symmetry of Ψ_t for even and odd n, also recorded in table I, is derived from the solution of the Schrödinger equation for the harmonic oscillator, $D_g^{(0)}$ for even n and $D_u^{(1)}$ for odd. The symmetry of Ψ_r, the wavefunctions of J for the rigid rotor are those of the hydrogen atom wavefunction for each point group, as recorded for the first four transitions in table I. The rotational degeneracy is $(2J + 1)$. The symmetry of the combined rotation translation wavefunctions depends on the product of the representations of the rotational and translational components. For even n this is the same as the rotational part of the complete wavefunction, but for odd n it is more complicated (table II). For odd n, the degeneracy of the rototranslational wavefunction is $3(2J + 1)$.

The allowed Raman transitions for each point group can now be calculated from eq. (3). An indication of the number of times the totally symmetric representation appears in the product of representations (3) is also the number of possible Raman transitions, degenerate and non-degenerate combined. Some representative ex-

Table III
Examples of products of representations

Point group	Transition		Symmetry representation	Relative intensity
T_d	$\Delta n = 0$, n even ,	$J = 0 \rightarrow J = 2$	$2A_1 + A_2 + 3E + 3T_1 + 4T_2$	2
	$\Delta n = 0$, n even ,	$J = 1 \rightarrow J = 3$	$5A_1 + 6A_2 + 11E + 15T_1 + 16T_2$	5
	$\Delta n = 0$, n odd ,	$J = 0 \rightarrow J = 2$	$12A_1 + 11A_2 + 23E + 33T_1 + 34T_2$	12
	$\Delta n = 1$, all n , even $n \rightarrow$ odd n	$J = 0 \rightarrow J = 3$,	$6A_1 + 5A_2 + 11E + 15T_1 + 16T_2$	6
	$\Delta n = 1$, n odd , odd $n \rightarrow$ even n	$J = 0 \rightarrow J = 3$,	$6A_1 + 5A_2 + 11E + 15T_1 + 16T_2$	6
C_1	$\Delta n = 0$, n even ,	$J = 0 \rightarrow J = 2$	45 A	45
	$\Delta n = 0$, n even ,	$J = 1 \rightarrow J = 3$	405 A	405
	$\Delta n = 0$, n odd ,	$J = 0 \rightarrow J = 2$	405 A	405
	$\Delta n = 0$, n odd ,	$J = 1 \rightarrow J = 3$	1701A	1701
	$\Delta n = 1$, even $n \rightarrow$ odd n	$J = 0 \rightarrow J = 3$,	189 A	189
	$\Delta n = 1$, odd $n \rightarrow$ even n	$J = 0 \rightarrow J = 3$.	189 A	189

amples are given in table III for T_d (spherical top symmetry) and C_1 (chiral symmetry).

The transition degeneracy and occurrences of the totally symmetric representation of the molecular point group increase steeply for odd n and increasing J.

A combination of quantised harmonic oscillation and rigid rotation produces a Raman spectrum which is full of new and interesting features, different for each point group.

These should be observable with high resolution for molecules trapped in lattices at low temperatures, thus building on the work of Ewing and co-workers for HD. The number of rototranslational degeneracies increases with decreasing molecular symmetry.

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References

[1] M.W. Evans, Chem. Phys. 127 (1988) 413.
[2] M.W. Evans, Chem. Phys. Letters 152 (1988) 33.
[3] R.L. Flurry Jr., Symmetry Groups, Theory and Chemical Applications (Prentice Hall, Englewood Cliffs, 1980).
[4] R.M. Hochstrasser, Molecular Aspects of Symmetry (Benjamin, New York, 1966).
[5] F.A. Cotton, Chemical Applications of Group Theory (Wiley Interscience, New York, 1963).
[6] H. Weyl, trans. H.P. Robertson, The Theory of Groups and Quantum Mechanics (Dover, New York, 1931).
[7] P.W. Atkins, Quantum Mechanics, 2nd Ed. (Oxford Univ. Press, Oxford, 1980).
[8] D.S. Urch, Orbitals and Symmetry (Penguin Books Ltd., Harmondsworth, 1970).
[9] G. Ewing, Accounts Chem. Research 2 (1969) 62.
[10] H. Friedmann and S. Kimel, J. Chem. Phys. 41 (1964) 2552.
[11] H. Friedmann and S. Kimel, J. Chem. Phys. 43 (1965) 3935.
[12] H. Friedmann and S. Kimel, J. Chem. Phys. 44 (1966) 4359.
[13] H. Friedmann and S. Kimel, J. Chem. Phys. 47 (1967) 3589.