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Quantum Mechanics of Rotating and Translating Molecules: Part 2, Far Infrared Spectrum of the Harmonic Oscillator/Rigid Rotor

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Abstract

Group theory is used in four dipolar point groups to determine the infrared selection rules and transition symmetries of a molecule whose dynamics are simultaneously those of the harmonic oscillator and rigid rotor. The motion is governed by the translational quantum number n of the harmonic oscillator and the quantum number J of the rigid rotor. The selection rules for the harmonic oscillator are modified from $\Delta n = \pm 1$ to $\Delta n = 0, \pm 1$. Those for the rigid rotor are changed from $\Delta J = 0, \pm 1$ in the absence of translation to (1) $\Delta J = 0, \pm 1, \pm 3$; $\Delta n = 0$, n odd; (2) $\Delta J = 0, \pm 1$; $\Delta n = 0$, n even; (3) $\Delta J = 0, \pm 2$, $\Delta n = \pm 1$; all n. The relative intensities of the rototranslational far infrared spectral lines are given for point groups C_{3v}, C_{2v}, C_{1h}, and C_1. The theory is in partial agreement with the experimental $\Delta J = 1, 2, 3, 4$ transitions observed in HD trapped in rare gas crystals at low temperature and with the selection rules for $C_{\infty v}$ symmetry obtained by Friedmann and Kimel.

1. Introduction

In part one of this series [1] a semiclassical theory of rotation and translation in rigid molecules was introduced which considered by group theory [2–6] the symmetry of wavefunctions generated by the simultaneous rotational and translational motion [7–10] of a molecule. In that work the rotational motion was assumed to be quantised, and the rigid rotor wave functions for each J quantum number expressed in terms of sums of irreducible representations of the molecular point group. In part one [1] the translational wave function was expressed through irreducible representations derived from the symmetry, $D_u^{(1)}$, of the classical linear velocity, v. Here, $D^{(0)}$, $D^{(1)}$, $D^{(2)}$... are irreducible representations of the 2-D rotation-reflection group $R_h(3)$. It was found that the symmetry of the wave function of combined rotation and translation, expressed through the product

$$\psi_{rt} = \psi_r \psi_t \qquad (1)$$

of component rotational (ψ_r) and translational (ψ_t) wave functions, led to the emergence of many more energy levels than is possible by consideration of "pure" rotation. The selection rules for pure rotation, i.e. $\Delta J = 0, \pm 1$, are modified by the product wave function (1) to

$$\Delta J = 0, \pm 1, \pm 3.$$

This result is achieved by assuming that the translational component ψ_t of the product (1) always has the classical

symmetry $D_u^{(1)}$, and closely resembles the experimental results reported by Ewing [11] in HD trapped in crystal cavities of rare gases. The experimental observations signal the disruption of the purely rotational quantum selection rule

$$\Delta J = 0, \pm 1$$

by rotation-translation effects, leading to absorptions in rotating and translating HD corresponding to $\Delta J = 0$, $+1$, $+2$, $+3$ and possibly $+4$. The last is not allowed, however, in the theory of part of this series [1], based on generally valid [2–6] group theoretical considerations. It is clear that translation-rotation effects are important and present in all molecular liquids and low temperature matrices, where some of the finer spectral details may be resolved.

The most important and detailed work on the quantum theory of combined molecular translation and rotation is still the series of papers produced in the sixties by Friedman and Kimel [12–15] for rare gas matrices of small diatomic and tetrahedral molecules. These papers used advanced second order perturbation theory to look at the spectral consequences of a hamiltonian of the type

$$H = H^{(0)} + aH_1 + a^2 H_{11} \equiv H^{(0)} + H', \qquad (2)$$

where H' is a perturbation term that accounts for rotation-translation coupling through the distance, a, between the molecular centre of mass and the centre of interaction. In qualitative terms the theory based on (2) introduces the translational quantum number n of the harmonic oscillator in addition to the usual rotational quantum number J. The term H' adds zero-point translational energy to the rotational states, and raises the J energy levels. $\Delta J = 2$ transitions are allowed by the theory. Apart from the usual $(2J + 1)$ degeneracy of the rotational levels the Friedmann Kimel theory (FK) introduces the degeneracy $1/2\,(n + 1)(n + 2)$ of the translational states modelled by a harmonic oscillator. Rotation-translation coupling lifts the total degeneracy

$$\tfrac{1}{2}(n + 1)(n + 2)(2J + 1)$$

of the (J, n) level of a rotor oscillating in a cell.

In this paper we employ group theory to investigate the existence of energies corresponding to a hamiltonian of type (2) and a perturbed rototranslational wave function of the type

$$\psi_i = \psi_i^{(0)} + \psi_i' \qquad (3)$$

for molecules whose motion is simultaneously described by the rigid rotor quantum number J and the harmonic oscillator quantum number n. There are therefore energy

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integrals of the type:

$$E_i^{(0)} = \langle \psi_i^{(0)} | H^{(0)} | \psi_i^{(0)} \rangle \tag{4}$$

$$E_i^{(1)} = \langle \psi_i^{(0)} | H' | \psi_i^{(0)} \rangle \tag{5}$$

$$E_i^{(2)} = \langle \psi_i' | H^{(0)} | \psi_i' \rangle \tag{6}$$

$$E_i^{(3)} = \langle \psi_i' | H' | \psi_i' \rangle \tag{7}$$

and so on, whose existence is determined [2] by the products of the group theoretical representations:

$$\Gamma(\psi_i^{(0)}) \times \Gamma(H^{(0)}) \times \Gamma(\psi_i^{(0)}) \tag{8}$$

and so on. These energy levels are infrared active if the product of representations

$$\Gamma(\psi_i) \times \Gamma(\mu_t) \times \Gamma(\psi_j) \tag{9}$$

includes the totally symmetric representation of the molecular point group at least once [2]. Here μ_t is the transition dipole. The number of occurrences of the totally symmetric representation in the product (9) gives the number of times the theoretically allowed far infrared absorption line occurs due to a transition between the rototranslational wave functions ψ_i and ψ_j for each of two (J, n) states i and j.

In the approximation (1) the symmetry of the rototranslational wavefunction is that of the product

$$\Gamma(\psi_{tr}) = \Gamma(\psi_t) \times \Gamma(\psi_r) \tag{10}$$

so that substitution of (10) in (9) leads to the result

$$\Gamma = \Gamma(\psi_{ti}) \times \Gamma(\psi_{ri}) \times \Gamma(\mu_t) \times \Gamma(\psi_{tj}) \times \Gamma(\psi_{rj}). \tag{11}$$

If Γ contains the totally symmetric representation of the point group at least once, then infrared absorption will occur, due to the influence of molecular rotation on translation. The number of totally symmetric representations in the product (11) gives the number of possible infrared absorption lines due to t/r coupling for a transition from quantum state i to quantum state j. The intensity of the transition from $i = |n, J\rangle$ to $j = |n', J'\rangle$ is proportional to the degeneracy $\frac{1}{2}n(n + 1)(2J + 1)$ and also to the number of totally symmetric representations in the product of group theoretical representations (11).

In this paper we are interested in the general symmetry of the problem, and use group theory to explore the harmonic oscillator/rotation spectrum for slected dipole point groups on the assumption that the symmetry of ψ_t is determined by the harmonic oscillator approximation, and that of ψ_r by the rigid rotor approximation.

2. Symmetry of translational wavefunctions from the harmonic oscillator

It is well known that the eigenfunctions of the translational harmonic oscillator have the symmetry of the Hermite polynomials of order n, whose orthogonality produces the selection rule $\Delta n = \pm 1$. The frequency separation between successive terms of the oscillator are the same, so all transitions occur at the same wavenumber when unaffected by rotation. For even n the representation $\Gamma(\psi_t)$ for all molecules is the totally symmetric representation. For odd n it is that of $D_u^{(1)}$, the translational coordinate itself.

3. Symmetry of rototranslational wavefunctions and selection rules

3.1. *Even n*

It follows that the symmetry of (10) of the rototranslational wavefunction for even n (including the ground state, $n = 0$) is the product of the totally symmetric representation of its translational component with the symmetry of the rotational component for a given J. The total symmetry is therefore identical with that of the rotational wavefunction itself.

The selection rules for the rigid rotor are derived from the Clebsch-Gordan formula

$$D^{(J)} \times D^{(J')} = D^{(J+J')} + \cdots + D^{|J-J'|}. \tag{12}$$

For infrared allowed rigid rotor absorptions this product must contain $D_u^{(1)}$, the symmetry of the transition dipole. This is possible from the right hand side of eq. (12) if and only if

$$\Delta J = 0, \pm 1. \tag{13}$$

For even n the symmetry of ψ_t is always the totally symmetric representation, so that

$$\Gamma_{tr}^{nJ} = \Gamma_t^n \times \Gamma_r^J = D_g^0 \times D^{(J)} = D^{(J)} \tag{14}$$

Therefore if the molecule is in the quantum state described by even n the J selection rules remain unchanged, i.e., are given by eq. (13).

3.2. *Odd n*

In this case the symmetry of ψ_t from the harmonic oscillator is $D_u^{(1)}$, which reduces as different irreducible representations for different molecules. In this case the Clebsch-Gordon expansion

$$(D_u^{(1)} \times D^{(J)}) \times (D_u^{(1)} \times D^{(J')}) \tag{15}$$

must contain the symmetry of the transition dipole, and this relaxes the selection rules of the rigid rotor to

$$\Delta J = 0, \pm 1, \pm 3 \tag{16}$$

as observed in HD/rare gas matrices and reported by Ewing [11]. For odd n therefore one immediate consequence of rotation-translation coupling is that the rigid rotor far infrared spectrum is supplemented by extra lines corresponding to $\Delta J = 3$. As shown in part 1, the intensity distributions for each envelope is strikingly different from that of the rigid rotor, and were given for most of the dipolar point groups.

Summary of selection rules for $\Delta n = 0$.

(I) For $\Delta n = 0$ and n odd; $\Delta J = 0, \pm 1, \pm 3$.
(II) For $\Delta n = 0$ and n even; $\Delta J = 0, \pm 1$.

3.3. *Selection rules for $\Delta n = \pm 1$*

For all n, the selection rule $\Delta n = \pm 1$ for the translational harmonic oscillator is derived from the orthogonality rules of the Hermite polynomials. For combined molecular rotation and translation the transition $\Delta n = \pm 1$ may be combined with a ΔJ and the rigid rotor selection rule $\Delta J = 0, \pm 1$ may be relaxed by the simultaneous $\Delta n = \pm 1$. In this case the product

$$(D_g^{(0)} \times D^{(J)}) \times (D_u^{(1)} \times D^{(J')}) \tag{17}$$

or the alternative

$$(D_u^{(1)} \times D^{(J)}) \times (D_g^{(0)} \times D^{(J')}) \tag{18}$$

Table I. *Occurrences of* A_1 *in product* (11) *for* C_{3v} *symmetry*

Selection rule	J transition							
	$J = 0 \rightarrow$ $J = 1$	$J = 1 \rightarrow$ $J = 2$	$J = 2 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 2$	$J = 1 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 0$	$J = 1 \rightarrow$ $J = 1$
(20), (odd n)	5	23	53	8	32	11	2	11
(21), (even n)	1	3	6	–	–	–	1	2
(22), even n to odd n	–	–	–	3	11	–	1	5
(22), odd n to even n	–	–	–	3	11	–	1	5

must contain the symmetry of the transition dipole, $D_u^{(1)}$. Product (17) arises from a $\Delta n = 1$ from a state $i \equiv (j,$ even $n)$ to a state $j \equiv (J',$ odd $n)$; and (18) from $i \equiv (J,$ odd $n)$ to $j \equiv (J',$ even $n)$. In either case the product of representations contains terms such as $D^{|J-J'|-1|}$, $D^{|J-J'|}$, $D^{|J-J'|+1}$, which contains $D_u^{(1)}$ if and only if:

(i) $\Delta J = 0, \pm 1, \pm 2$;

(ii) the rotational part of (16) and (17), i.e., $D^{(J)} \times D^{(J')}$ is g.

The second argument means that rotational transitions $\Delta J = \pm 1$ between adjacent g and u rotational wavefunction symmetries cannot be allowed. This leaves the simultaneous selection rules as

$$\Delta n = \pm 1; \quad \Delta J = 0, \pm 2. \tag{19}$$

It is interesting to note that Friedmann and Kimel [12–15] also found the rule $\Delta J = 0, \pm 2$ using second order perturbation theory. This result was also reviewed by Ewing [11]. However, the FK result was found for the special case of simmple diatomics in rare gas matrices. The selection rules given in this paper are derived purely from symmetry, and are applicable to all molecular point groups in any environment that supports interaction between molecular rotation and harmonic oscillation.

4. Occurrences of the totally symmetric representation in the product of representations (11)

This number can now be examined by group theory for each of the above sets of selection rules for the various dipolar molecular point groups. In this section it is calculated for the cases:

(1) $\Delta n = 0; \Delta J = 0, \pm 1, \pm 3; n$ odd   (20)

(2) $\Delta n = 0; \Delta J = 0, \pm 1; n$ even;   (21)

(3) $\Delta n = 1; \Delta J = 0, \pm 2;$ all n;   (22)

for the dipolar point groups C_{3v} (symmetric top); C_{2v} (asymmetric top); C_{1h} (planar asymmetric top) and C_1 (lowest symmetry, chiral). $\Gamma(\mu_t)$ reduces within each point group as the totally symmetric representation of the group. In each case rules (20) to (22) allow a rich spectrum of absorptions even in the relatively simple harmonic oscillator approximation. It may be expected that rotation-translation coupling also produces anharmonicity in the oscillation of the centre of mass, but that is not pursued here.

4.1. *The C_{3v} point group*

In part 1 of this series, the occurrences of the totally symmetric representation (A_1) of this group were calculated from group theory applied to the product (11). In that work the symmetry of the molecular translational velocity, v, was taken as the classical $D_u^{(1)}$. In this work we use the methods of part 1 to investigate the number of occurrences in product (11) of the totally symmetric representation A_1 for the selection rules (20), (21) and (22). The absorptions corresponding to (20), (21), and (22) are best resolved in rare gas matrices at low temperatures, entrapping dipolar molecules which are simultaneously rotating and translating. At low temperatures only the first few J lines are of interest. The occurrences of A_1 in the product (11) are summarized in Table I in this case for each of the selection rules (20) to (22).

4.2. *The C_{2v} point group*

The occurrences of the totally symmetric representation, A_1, of this group from product (11) for some J translations are shown in Table II. It can be seen from a comparison of Tables I and II that there are more occurrences for each transition for C_{2v} symmetry (asymmetric top) than for C_{3v} symmetry (the symmetric top). This means that the allowed rototranslational intensities for the asymmetric top are greater than their equivalents for the symmetric top.

Table II. *Occurrences of* A_1 *in product* (11) *for* C_{2v} *symmetry*

Selection rule	J transition							
	$J = 0 \rightarrow$ $J = 1$	$J = 1 \rightarrow$ $J = 2$	$J = 2 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 2$	$J = 1 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 0$	$J = 1 \rightarrow$ $J = 1$
(20), (odd n)	7	34	79	12	48	16	3	21
(21), (even n)	1	4	9	–	–	–	1	3
(22), even n $\rightarrow$ odd n	–	–	–	4	16	–	1	7
(22), odd n $\rightarrow$ even n	–	–	–	4	16	–	1	7

Table III. *Occurrences of* A′ *in product* (11) *for* C_{1h} *symmetry*

| Selection rule | J transition | | | | | | | |
	$J = 0 \rightarrow$ $J = 1$	$J = 1 \rightarrow$ $J = 2$	$J = 2 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 2$	$J = 1 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 0$	$J = 1 \rightarrow$ $J = 1$
(20), (odd n)	14	68	158	23	95	32	5	4
(21), (even n)	2	8	18	–	–	–	1	5
(22), (even n to odd n)	–	–	–	8	11	–	2	14
(22), (odd n to even n)	–	–	–	8	11	–	2	14

Table IV. *Occurrences of* A *in product* (11) *for* C_1 *symmetry*

| Selection rule | J transition | | | | | | | |
	$J = 0 \rightarrow$ $J = 1$	$J = 1 \rightarrow$ $J = 2$	$J = 2 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 2$	$J = 1 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 3$	$J = 0 \rightarrow$ $J = 0$	$J = 1 \rightarrow$ $J = 1$
(20), (odd n)	27	135	315	45	189	63	9	
(21), (even n)	3	15	35	–	–	–	1	
(22), (even n to odd n)	–	–	–	15	63	–	3	
(22), (odd n to even n)	–	–	–	15	63	–	3	

4.3. *The* C_{1h} *and* C_1 *point groups*

The C_{1h} is a lower symmetry than the C_{2v} and both describe asymmetric top molecules. The C_1 point group is that of lowest molecular symmetry, and describes chiral molecules such as ChClBrF. It can be seen across Tables I to IV that the occurrences of the relevant totally symmetric representations, A_1, A_1, A′, and A respectively, increase as the molecular symmetry decreases.

5. Discussion

The result of the symmetry arguments of this paper may be summarized graphically in Fig. 1. The basic assumption (1) results in a relaxation of both the harmonic oscillator and rigid rotor selection rules, and results in new rototranslational selection rules in agreement with the observations described by Ewing [11], and with the theoretical work of Friedmann and Kimel [12–15] on linear dipolar molecules. The occurrences of the totally symmetric representations of the four point groups studied in this paper provide an approximation to the intensity distribution of each set of lines. The intensity is expected to be relatively greater for the least symmetric point group than for the most symmetric. The effect of assumption (1) on the selection rules can be summarized as follows.

(1) The translational selection rules of the harmonic oscillator are changed from $\Delta n = \pm 1$ to $\Delta n = 0, \pm 1$.

(2) The rules for the rigid rotor are modified considerably as described in the text.

Therefore, the spectrum expected from rototranslation as opposed to pure rotation (or harmonic oscillation) is that of Fig. 1, where many new infrared active transitions become possible. The complete spectrum is a superposition of those of Figs. 1(a), (b) and (c).

A great deal of further investigation is required on small molecules trapped at low temperatures in clathrate type lattices to verify experimentally the theoretical spectrum of Fig. 1. Some exploratory work of this nature has been completed by Davies [16] and the absorptions have been described as rattling modes [17]. A clear experimental description of rototranslation is available in a review paper by Ewing [11],
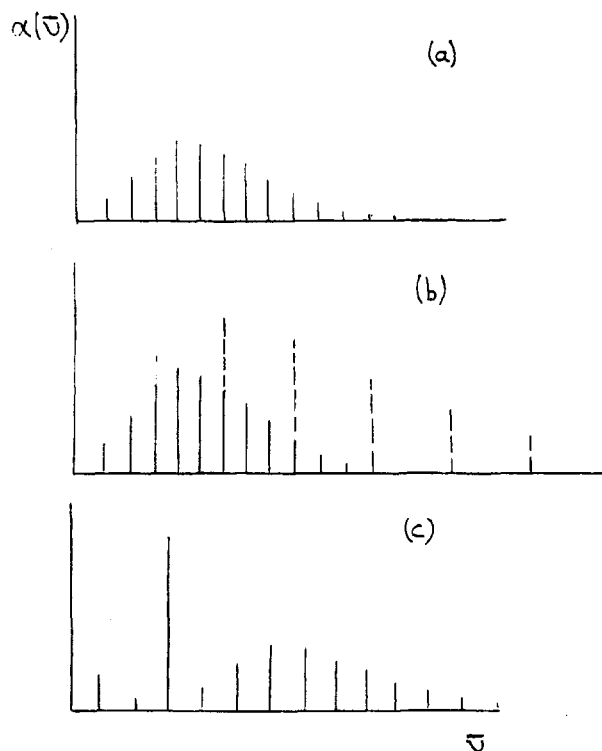

Fig. 1. (a) The quantum absorptions, $\Delta J = 1$, of the rigid rotor. (b) The $\Delta n = 0$, $\Delta J = 3$ distribution allowed by combined rotation and translation. (c) The $\Delta n = 1$, $\Delta J = \pm 2$ distribution from combined rotation and translation. The complete rototranslational spectrum is a combination of (a) to (c).

referring to the far infrared spectrum of HD in rare gas crystals at low temperature.

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