273

IL NUOVO CIMENTO VOL. 11 D, N. 9 Settembre 1989

The Quantum Mechanics of Rotating and Translating Molecules: Semi-Classical Treatment. - I.

M. W. EVANS

Dept. of Chemistry, Bourne Laboratory, Royal Holloway and Bedford New College
University of London, Egham Hill - Egham, Surrey TW20 OEW, England, U.K.

(ricevuto il 19 Settembre 1988; manoscritto revisionato ricevuto il 30 Gennaio 1989)

Summary. — The emergence by classical computer simulation of definitive evidence for statistical correlation between molecular rotation and translation leads to a new appraisal of the quantum structure of rotational absorption in the microwave and far infrared. The classical correlation implies that the accepted theory of «pure rotational» quantum absorption is only a first approximation. The translation of a molecule in some environments affects its own quantized absorption due to rotation. The number of allowed quantum transitions is increased from the accepted theoretical $\Delta J = \pm 1$ to $\Delta J = \pm 1, \pm 2, \pm 3$ for all dipolar molecules. These results are obtained using group theory, which also predicts that translation rotation effects increase the number of allowed transitions for each J quantum number and therefore affect the intensity distribution of the absorption lines. These results modify fundamentally the accepted theory of quantized rotation. Theoretically, the well-known $\Delta J = 1$ distribution is supplemented by further distributions at $\Delta J = 2$ and $\Delta J = 3$.

PACS 31.10 – General theory of electronic structure, electronic transitions, and chemical binding.

1. – Introduction.

A series of recent computer simulations (1-5) has revealed a set of nonvanishing time cross-correlation functions in ensembles of interacting molecules. These

---

(1) M. W. EVANS: *Phys. Rev. Lett.*, 50, 351 (1983).

(2) M. W. EVANS and G. J. EVANS: *Advances in Chemical Physics*, Vol. 63 (Wiley Interscience, New York, N.Y., 1985).

(3) M. W. EVANS, G. C. LIE and F. CLEMENTI: *J. Chem. Phys.*, 87, 6040 (1987).

(4) M. W. EVANS, K. REFSON, K. N. SWAMY, G. C. LIE and E. CLEMENTI: *Phys. Rev. A*, 36, 3935 (1987).

(5) M. W. EVANS and G. J. EVANS: *J. Mol. Liq.*, 36, 293 (1987).

link statistically the fundamental molecular rotational and translational diffusion from a classical point of view. Subsequently, the computer simulations have been verified in detail by a fundamentally new development (6) in statistical mechanics which is based on the ideas of group theory and on the idea that ensemble averages in the molecule fixed frame can be treated in terms of point group theory. This has developed into the subject of «group-theoretical statistical mechanics» (g.t.s.m.).

In this paper the quantum-mechanical theory of combined molecular rotation and translation is developed from the above classical basis, *i.e.* the existence from computer simulation of the cross correlation function $\langle \boldsymbol{v}(t)\boldsymbol{J}_c^T(0)\rangle$ in the molecule fixed frame (x, y, z). Here $\boldsymbol{v}$ is the centre-of-mass linear velocity and $\boldsymbol{J}_c$ the molecular angular momentum. In sect. 1 the groundwork for the new treatment is given briefly, sect. 2 deals with selection rules and intensities in the far infra red and sect. 3 gives results for some representative point groups. Section 4 is a discussion and survey of spectral implications.

2. – Fundamental concepts and definitions.

We seek the solution of the Schrödinger equation for a rigid, nonvibrating, molecule which is simultaneously rotating and translating and in which one motion implicitly influences the other. We assume that the classical time cross correlation function $\langle \boldsymbol{v}(t)\boldsymbol{J}_c(0)\rangle$ exists in frame (x, y, z) in an ensemble of such molecules. Experimental conditions are assumed to be optimized for the observation of quantum structure, for example in low-temperature rare-gas lattices in which the rotating and translating molecules are encaged. The treatment that follows is based on standard group theory (7-11) applied to this experimental situation. The rotational motion is treated quantum-mechanically and the translational motion classically, so that our model is in this sense a semi-classical approximation. Selection rules and relative absorption intensities are derived on the grounds of symmetry for each point group. The basic laws of quantum mechanics apply as usual and the symmetry of three-dimensional space

---

(6) D. H. WHIFFEN: *Mol. Phys.*, 63, 1053 (1988).

(7) P. L. FLURRY jr.: *Symmetry Groups, Theory and Chemical Applications* (Prentice-Hall Inc., Englewood Cliffs, N.J., 1980).

(8) R. M. HOCHSTRASSER: *Molecular Aspects of Symmetry* (W. A. Benjamin, Inc., New York, N.Y., 1966).

(9) F. A. COTTON: *Chemical Applications of Group Theory* (Wiley Interscience, New York, N.Y., 1963).

(10) H. WEYL (translation by H. P. ROBERTSON): *The Theory of Groups and Quantum Mechanics* (Dover, New York, N.Y., 1931).

(11) J. A. SALTHOUSE and M. J. WARE: *Point Group Character Tables* (Cambridge University Press, Cambridge, 1972), p. 55.

is designated by the rotation reflection(7) point group $R_h(3)$ whose irreducible representations are denoted by the D representations

$$D_g^{(0)}, D_g^{(1)}, D_g^{(n)}, \qquad D_u^{(0)}, D_u^{(1)}, D_u^{(n)}.$$

Products of D representations are given by the Clebsch-Gordan theorem

$$D^{(j)}D^{(k)} = D^{(j+k)} + D^{(j+k-1)} + \ldots + D^{(|j-k|)}. \tag{1}$$

The translational motion of the molecular centre of mass is assumed to reduce in $R_h(3)$ as the polar vector representation $D_u^{(1)}$ of classical mechanics, so that the quantum states are infinitely close together from $-\infty$ to ∞. (Later work will improve on this by considering fully quantized translational harmonic oscillation superposed on quantized rotation.) The molecular angular momentum is assumed to be fully quantized and the rotational quantum states are defined in terms of the irreducible representation of the molecular point group, which is determined by the Hamiltonian of the system.

The irreducible representation of the rototranslational wave function for a molecular point group is the product of those for rotation and translation:

$$\Gamma(\psi) = \Gamma(|vJ\rangle) = \Gamma(|v\rangle)\Gamma(|J\rangle), \tag{2}$$

and a transition from state i to state f is allowed if $\Gamma(\psi_i)\Gamma(\psi_f)$ contains the irreducible representation $\Gamma(M)$ of the molecular dipole moment $\boldsymbol{M}$ within the point group of the molecule.

3. – Selection rules and intensities.

We first note that «pure rotation» implies the classical result

$$\langle \boldsymbol{v}(t)\boldsymbol{J}_c^{\mathrm{T}}(0)\rangle_{(x,y,z)} = 0, \tag{3}$$

for all t, which is possible only when the Hamiltonian is purely kinetic, as in the «infinitely» dilute gas. A nonvanishing potential energy term in the Hamiltonian leads immediately to (1-5)

$$\langle \boldsymbol{v}(t)\boldsymbol{J}_c^{\mathrm{T}}(0)\rangle_{(x,y,z)} \neq 0, \qquad 0 < t < \infty, \tag{4}$$

for all dipolar molecules.

Selection rules in the limit of «pure» quantized rotation. These are derived from the Clebsch-Gordan formula. If the initial rotational quantum number is J

and the final is J', then the symmetry restrictions on radiation-induced transitions between purely rotational energy levels are obtained from the requirement that $\Gamma(\psi_J)\Gamma(\psi'_J)$ contain $D_u^{(1)}$. This implies

$$D_g^{(J)} D_u^{(J')} = D_u^{(J+J')} + \ldots + D_u^{|J-J'|} \tag{5}$$

must contain $D_u^{(1)}$. This is because the symmetry of the molecular dipole moment is $D_u^{(1)}$. Requirement (5) can only be met if

$$\Delta J = \pm 1\,, \tag{6}$$

which implies transitions from g to u or from u to g.

Selection rules for quantized rototranslation. In this case the product

$$(D_u^{(1)} D_g^{(J)})(D_u^{(1)} D_u^{(J')}) \tag{7}$$

must contain $D_u^{(1)}$, the symmetry of the molecular dipole moment. We have

$$(D_u^{(1)} D_g^{(J)})(D_u^{(1)} D_u^{(J')}) = (D_g^{(0)} + D_g^{(1)} + D_g^{(2)})(D_u^{|J+J'|} + \ldots + D_u^{|-J'|})\,. \tag{8}$$

This product contains the terms $D_u^{|J-J'|}$; $D_u^{||J-J'|-1|}$ and $D_u^{||J-J'|-2|}$ as part of its expansion using the Clebsch-Gordan formula. These contain $D_u^{(1)}$ if and only if

$$\Delta J = \pm 1, \pm 2, \pm 3\,. \tag{9}$$

The infra-red selection rules for rototranslation are, therefore,

$$\Delta n = 0 \text{ (translation)}, \qquad \Delta J = \pm 1, \pm 2, \pm 3 \text{ (rotation)}, \tag{10}$$

i.e., as soon as the «infinitely» dilute gas is compressed infinitesimally, the absorption spectrum of combined and quantized rotation and translation contains absorptions corresponding to $\Delta J = 1, 2, 3$ for all dipolar molecules.

A similar result has been obtained by Friedmann and Kimel (12) in the special case of HD translating and rotating in a harmonic translational potential. Experimental evidence for the extra allowed ΔJ lines has been presented by Ewing (13).

There seems to be no other study of quantized absorption due to simultaneous molecular rotation and translation. It is clear from (10) however that in quantum mechanics the influence of one type of motion on the other is fundamental,

---

(12) H. FRIEDMANN and S. KIMEL: *J. Chem. Phys.*, 47, 3589 (1967).
(13) G. EWING: *Acc. Chem. Res.*, 2, 168 (1969).

adding observable quantized features in the microwave and far infra red. These correspond to $\Delta J = 2, 3$ in the present semi-classical model. The traditional $\Delta J = 1$ of pure rotation is also affected and the extra absorptions predicted in this paper may have been observed (14) in the far-infra-red spectrum of compressed gaseous chlorotrifluoromethane. These were originally attributed (14) to induced absorption (15), but may well have come from a combination of rotation and translation in the compressed gas.

Intensity of quantum absorptions: pure rotation. The intensity distribution of the purely rotational $\Delta J = 1$ absorptions in the microwave/far infra red is determined partly by the equilibrium distribution of «purely» rotational quantum states, and partly by the number of times the totally symmetric representation occurs in the product

$$\Gamma(\psi_J)\Gamma(M)\Gamma(\psi_{J'}). \tag{11}$$

For example, if we take the low-symmetry group C_1, one of whose members is CHBrClF, the symmetry is as follows:

$$\Gamma(M) = A\,, \quad \Gamma(\psi_{J=0}) = A\,, \quad \Gamma(\psi_{J=1}) = 3A\,, \ldots .$$

The product of representations (11) is, therefore,

1) $3A$ for $J = 0 \to J = 1$,
2) $15A$ for $J = 1 \to J = 2$

and so on.

The number of totally symmetric representations, A, in (11) rapidly increases with J in the transition $J \to J+1$. There are $(2J+1)\,(2J-1)$ totally symmetric representations for the transition $(J-1) \to J$. The intensity of each J line of the C_1 «pure» rotational spectrum is given by the product multiplied by the Maxwell-Boltzmann distribution in the absence of other factors such as J degeneracy and nuclear spin coupling.

Intensity distribution in combined rotation and translation. The product (11) of irreducible representations is now modified to

$$\Gamma(|v\,J_i\rangle)\Gamma(M)\Gamma(|v\,J_f\rangle) \tag{12}$$

with selection rules given by (10).

---

(14) M. W. Evans and G. J. Davies: *J. Chem. Soc. Faraday Trans. 2*, 71, 1275 (1975).

(15) M. W. Evans, G. J. Evans, W. T. Coffey and P. Grigolini: *Molecular Dynamics* (Wiley Interscience, New York, N.Y., 1982).

In the point group C_1 we now have

$$\Gamma(M) = A\,, \qquad \Gamma(|vJ=0\rangle) = 3A\,, \qquad \Gamma(|vJ=n\rangle) = 3(2n+1)A\,.$$

Product (12) for $\Delta J = 1$. 1) $27A$ for $J=0 \rightarrow J=1$, 2) $135A$ for $J=1 \rightarrow J=2$, 3) $315A$ for $J=2 \rightarrow J=3$, etc.

Product (12) for $\Delta J = 2$. 1) $45A$ for $J=0 \rightarrow J=2$, 2) $189A$ for $J=1 \rightarrow J=3$, etc.

The occurrences of the totally symmetric representation, A, are increased by a factor of nine for $\Delta J = 1$, and are $27:135:315, \ldots, 9(2J+1)(2J-1)$. The series for $\Delta J = 3$ is 63.... These are weighted by other factors (7) such as the Maxwell-Boltzmann equilibrium distribution of both molecular rotational and translational states and their degeneracies.

The observable effect of molecular translation on rotation in quantum mechanics is to promote a finite number of new ΔJ allowed transitions, each with an increased number of allowed totally symmetric representations in the product (12) as compared with (11), the equivalent of «pure» rotation.

4. – Examples for the C_n and C_{nv} point groups.

These are the point groups of the class of chiral molecules (C_n) and dipolar molecules (C_{nv}). Examples (9) are CHFClBr (C_1), diphenylfluoroboron (C_2), triphenylarsenic (C_3), tetraphenylcyclobutadiene (C_4), hexaphenylbenzene (C_6). Of these only the first two are dipolar, but there may be examples of other C_A point groups which are dipolar.

The first stage in our treatment is to describe $D^{(0)}, D^{(1)}, \ldots, D^{(n)}$ in terms of the irreducible representations of each point group. This is carried out in appendix A. The second stage finds the symmetry of the rototranslational wave functions $|vJ=0\rangle$, $|vJ=1\rangle$, $|vJ=2\rangle$, and evaluates the product (12) for each point group. This involves the use of the multiplication properties of irreducible representations given in appendix B. For each point group is listed the symmetry of the rototranslational wavefunctions up to $|vJ=3\rangle$, and the number of occurrences from (12) of the totally symmetric representation for the point group for $\Delta J = 1$, $\Delta J = 2$ and $\Delta J = 3$.

The C_1 point group ($\Gamma(M) = A$).

1) The irreducible representations of the first few rototranslational wave functions are

$$\Gamma(|vJ=0\rangle) = A\,, \qquad \Gamma(|vJ=1\rangle) = 9A\,,$$

$$\Gamma(|vJ=2\rangle) = 15A\,, \qquad \Gamma(|vJ=3\rangle) = 21A\,.$$

2) The product of representations (12) is given in sect. 2.

The C_2 point group $(\Gamma(M) = A)$

1)
$$\begin{cases} \Gamma(|vJ=0\rangle) = A + 2B\,, \\ \Gamma(|vJ=1\rangle) = 5A + 4B\,, \\ \Gamma(|vJ=2\rangle) = 7A + 8B\,, \\ \Gamma(|vJ=3\rangle) = 11A + 10B\,. \end{cases}$$

2) The product of representations (12).

For $\Delta J = 1$

$$\left.\begin{aligned} &J=0\to J=1:\ 13A+14B \\ &J=1\to J=2:\ 67A+68B \\ &J=2\to J=3: 157A+158B \end{aligned}\right\}\ 13:67:157:\ldots\,.$$

For $\Delta J = 2$

$$\left.\begin{aligned} &J=0\to J=2:\ 23A+22B \\ &J=1\to J=3:\ 95A+94B \end{aligned}\right\}\ 23:95:\ldots\,.$$

For $\Delta J = 3$

$$J=6\to J=3:\ 31A+32\ B;\qquad 31:\ldots\,.$$

The C_3 point group $(\Gamma(M) = A)$

1)
$$\begin{cases} \Gamma(|vJ=0\rangle) = A + E\,, \\ \Gamma(|vJ=1\rangle) = 3A + 3E\,, \\ \Gamma(|vJ=2\rangle) = 5A + 5E\,, \\ \Gamma(|vJ=3\rangle) = 7A + 7E\,. \end{cases}$$

2) The product of representations (12).

For $\Delta J=1$

$$\left.\begin{array}{l} J=0\rightarrow J=1:\quad 9A+\ \ 9E\\ J=1\rightarrow J=2:\ 45A+\ 45E\\ J=2\rightarrow J=3: 105A+105E\end{array}\right\}\ 13:67:105:\dots\,.$$

For $\Delta J=2$

$$\left.\begin{array}{l} J=0\rightarrow J=2:\ 15A+15E\\ J=1\rightarrow J=3:\ 63A+63E\end{array}\right\}\ 15:63:\dots\,.$$

For $\Delta J=3$

$$J=0\rightarrow J=3:\ 21A+21E\ ;\quad 21:\dots\,.$$

The C_4 *point group* $(\Gamma(M)=A)$.

1)
$$\left\{\begin{array}{l} \Gamma(|vJ=0\rangle)=\ \ A+E\,,\\ \Gamma(|vJ=1\rangle)=3A+2B+2E,\\ \quad |vJ=2\rangle=3A+4B+4E,\\ \quad |vJ=3\rangle=4A+5B+6E.\end{array}\right.$$

2) The product of representations (12).

For $\Delta J=1$

$$\left.\begin{array}{l} J=0\rightarrow J=1:\quad 7A+\ 6B+\ 7E\\ J=1\rightarrow J=2:\ 33A+34B+34E\\ J=2\rightarrow J=3:\ 80A+79B+94E\end{array}\right\}\ 7:33:80:\dots\,.$$

For $\Delta J=2$

$$\left.\begin{array}{l} J=0\rightarrow J=2:\ 11A+12B+11E\\ J=1\rightarrow J=3:\ 34A+35B+48E\end{array}\right\}\ 11:34:\dots\,.$$

For $\Delta J = 3$

$$J=0\to J=3:\ 16A+17B+15E;\ 16:\dots .$$

The C_6 *point group* $(\Gamma(M)=A)$.

$$1)\qquad \begin{cases} |vJ=0\rangle = A+E_1, \\ |vJ=1\rangle = 3A+2E_1+E_2, \\ |vJ=2\rangle = 3A+2B+2E_1+2E_2, \\ |vJ=3\rangle = 3A+4B+3E_1+4E_2. \end{cases}$$

2) The product of representations (12).

For $\Delta J = 1$

$$\left.\begin{array}{ll} J=0\to J=1: & 7A+\ 2B+\ 6E_1+\ 3E_2 \\ J=1\to J=2: & 25A+20B+24E_1+21E_2 \\ J=2\to J=3: & 67A+38B+66E_1+39E_2 \end{array}\right\}\ 7:25:67:\dots .$$

For $\Delta J = 2$

$$\left.\begin{array}{ll} J=0\to J=2: & 9A+\ 6B+\ 7E_1+\ 7E_2 \\ J=1\to J=3: & 33A+30B+34E_1+29E_2 \end{array}\right\}\ 9:33:\dots .$$

For $\Delta J = 3$

$$J=0\to J=3:\ 13A+7B+10E_1+11E_2;\ \ 13:\dots .$$

The C_{2v} *group* $(\Gamma(M)=A_1)$.

$$1)\qquad \begin{cases} \Gamma(|vJ=0\rangle) = A_2+\ B_2+\ B_1, \\ \Gamma(|vJ=1\rangle) = 2A_1+3A_2+2B_1+2B_2, \\ \Gamma(|vJ=2\rangle) = 3A_1+4A_2+4B_1+4B_2, \\ \Gamma(|vJ=3\rangle) = 5A_1+6A_2+5B_1+5B_2. \end{cases}$$

2) The product of representations (12).

$\Delta J = 1$

$$\left.\begin{aligned} J=0\rightarrow J=1&:\ \ 7A_1+\ \ 6A_2+\ \ 7B_1+\ \ 7B_2\\ J=1\rightarrow J=2&:\ 34A_1+33A_2+34B_1+34B_2\\ J=2\rightarrow J=3&:\ 79A_1+78A_2+79B_1+79B_2\end{aligned}\right\}\ 7:34:79:\ldots\,.$$

$\Delta J = 2$

$$\left.\begin{aligned} J=0\rightarrow J=2&:\ 12A_1+11A_2+11B_1+11B_2\\ J=1\rightarrow J=3&:\ 48A_1+47A_2+47B_1+47B_2\end{aligned}\right\}\ 12:48:\ldots\,.$$

$\Delta J = 3$

$$J=0\rightarrow J=3:\ 16A_1+15A_2+16B_1+16B_2;\quad 16:\ldots\,.$$

The C_{3v} *point group* $(\Gamma(M)=A_1)$; *simmetric top.*

$$1)\qquad \begin{cases} \Gamma(|vJ=0\rangle)=\ \ \ \ \ \ A_2+\ \ E\,,\\ \Gamma(|vJ=1\rangle)=\ \ A_1+2A_2+3E\,,\\ \Gamma(|vJ=2\rangle)=2A_1+3A_2+5E\,,\\ \Gamma(|vJ=3\rangle)=3A_1+4A_2+7E\,.\end{cases}$$

2) The product of representations (12).

$\Delta J = 1$

$$\left.\begin{aligned} J=0\rightarrow J=1&:\ \ 5A_1+\ \ 4A_2+\ \ \ 9E\\ J=1\rightarrow J=2&:23A_1+22A_2+\ \ 45E\\ J=2\rightarrow J=3&:53A_1+52A_2+105E\end{aligned}\right\}\ 5:23:53:\ldots\,.$$

$\Delta J = 2$

$$\left.\begin{aligned} J=0\rightarrow J=2&:\ \ 8A_1+\ \ 7A_2+\ \ 15E\\ J=1\rightarrow J=3&:32A_1+31A_2+\ \ 63E\end{aligned}\right\}\ 8:32:\ldots\,.$$

$\Delta J = 3$

$$J=0\rightarrow J=3:11A_1+10A_2+\ \ 21E;\quad 11:\ldots\,.$$

The dipolar point group C_{1h} ($\Gamma(\boldsymbol{m}) = A'$).

$$1)\qquad \begin{cases} |vJ=0\rangle = A' + 2A'', \\ |vJ=1\rangle = 4A' + 5A'', \\ |vJ=2\rangle = 7A' + 8A'', \\ |vJ=3\rangle = 10A' + 11A''. \end{cases}$$

2) The product of representations (12).

$\Delta J = 1$

$$\left.\begin{aligned} J=0\to J=1&:\ 14A' + 13A'' \\ J=1\to J=2&:\ 68A' + 67A'' \\ J=2\to J=3&:\ 158A' + 157A'' \end{aligned}\right\}\ 14:68:158:\dots\,.$$

$\Delta J = 2$

$$\left.\begin{aligned} J=0\to J=2&:\ 23A' + 22A'' \\ J=1\to J=3&:\ 95A' + 94A'' \end{aligned}\right\}\ 23:95:\dots\,.$$

$\Delta J = 3$

$$J=0\to J=3:\ 32A' + 31A''; \qquad 32:\dots\,.$$

5. – Discussion.

On the basis of the classical result (12) group theory has been used to work out some of the many expected spectral consequences of solutions of the Schrödinger equation for combined quantized rotation and translation. The results for selection rules and intensities are given in the preceding section.

We come to the conclusion that the accepted theory of «pure» rotational quantum absorption in the microwave and far infrared is only a first approximation to the results expected for combined rotation and translation. Specifically, the centre-of-mass translation of a molecule affects its own quantized rotation in an observable way. The effect of translation is to increase the number of allowed J transitions from $\Delta J = 0, \pm 1$ to $\Delta J = 0, \pm 1, \pm 2, \pm 3$ for all dipolar molecules. Therefore, absorption lines due to $\Delta J = 2$ and $\Delta J = 3$ become observable and the intensity distribution of $\Delta J = 1$ is changed. Furthermore, group theory predicts that translation increases the number of totally symmetric representations of the product (21) for all allowed ΔJ transitions.

The irreducible representations in the frame (x, y, z) for the time cross correlation functions $\langle v(t)\boldsymbol{J}^{\mathrm{T}}=0(0)\rangle$; $\langle v(t)\boldsymbol{J}^{\mathrm{T}}=1(0)\rangle$; $\langle v(t)\boldsymbol{J}^{\mathrm{T}}=2(0)\rangle$ etc. are the same as those for the rototranslational wave functions $|vJ=0\rangle$, $|vJ=1\rangle$, $|vJ=2\rangle$. Here $\boldsymbol{J}=n(0)$ denotes quantized angular momentum in the state $J=n$ at time $t=0$. The classical c.c.f. can be seen as the expectation value of the Liouville operator in the state $|vJ=n\rangle$ and so there are many expectation values in quantum mechanics corresponding to the classical result (12).

* * *

The University of Lancaster is thanked for an Honorary Fellowship.

APPENDIX A

This appendix gives the reductions of $D_g^{(0)}, \ldots, D_g^{(n)}$ and $D_u^{(0)}, \ldots, D_u^{(n)}$ in terms of the irreducible representations of most of the dipolar molecular point groups; see table I.

TABLE I. – *Mappings of some of the dipolar point groups onto some $R_h(3)$ irreducible representations.*

	Point group							
	C_1	C_2	C_3	C_4	C_6	C_{2v}	C_{3v}	C_{1h}
$D_g^{(0)}$	A	A	A	A	A	A_1	A_1	A'
$D_u^{(0)}$	A	A	A	A	A	A_2	A_2	A''
$D_g^{(1)}$	$3A$	$A+2B$	$A+E$	$A+E$	$A+E_1$	A_2+B_1+ $+B_2$	A_2+E	$A'+2A''$
$D_u^{(1)}$	$3A$	$A+2B$	$A+E$	$A+E$	$A+E_1$	A_1+B_1+ $+B_2$	A_1+E	$2A'+A''$
$D_g^{(2)}$	$5A$	$3A+2B$	$A+2E$	$A+E+$ $+2B$	$A+E_1+$ $+E_2$	$2A_1+A_2+$ $+B_1+B_2$	A_1+2E	$3A'+2A''$
$D_u^{(2)}$	$5A$	$3A+2B$	$A+2E$	$A+E+$ $+2B$	$A+E_1+$ $+E_2$	A_1+2A_2+ $+B_1+B_2$	A_2+2E	$2A'+3A''$
$D_g^{(3)}$	$7A$	$3A+4B$	$3A+2E$	$2A+E+$ $+3B$	$A+E_1+$ $+E_2+2B$	A_1+2A_2+ $+2B_1+2B_2$	A_1+2A_2+ $+2E$	$3A'+4A''$
$D_u^{(3)}$	$7A$	$3A+4B$	$3A+2E$	$2A+E+$ $+3B$	$A+E_1+$ $+E_2+2B$	$2A_1+A_2+$ $+2B_1+2B_2$	$2A_1+A_2+$ $+2E$	$4A'+3A''$

APPENDIX B

This appendix provides the rules for products of Mulliken's symbols for irreducible representations for all the usual point groups used in spectroscopic theory.

General Rules $A\times A=A$; $B\times B=A$; $A\times B=B$; $A\times E=E$; $B\times E=E$; $A\times T=T$; $B\times T=T$; $A\times E_1=E_1$; $A\times E_2=E$; $B\times E_1=E_2$; $B\times E_2=E_1$; $'x'='$; $'x''=''$; $''x''='$.

Subscripts $1\times 1=1$; $2\times 2=1$; $1\times 2=2$; except for D_2 and D_{2h}, where $1\times 2=3$; $2\times 3=1$; $g\times g=u\times u=g$; $g\times u=u\times g=u$.

Doubly degenerate

1) For C_3; C_{3h}; C_{3v}; D_3; D_{3h}; D_{3d}; C_6; C_{6v}; D_6; D_{6h}; S_6; O; O_h; T; T_d; T_h; $E_1\times E_1=E_2\times E_2=A_1+A_2+A_2$; $E_1\times E_2=B_1+B_2+E_1$.

2) For C_4; C_{4v}; C_{4h}; D_{2d}; D_4; S_4; $E\times E=A_1+A_2+B_1+B_2$.

Triply degenerate

1) For T_d; O; O_h; $E\times T_1=E\times T_2=T_1+T_2$; $T_1\times T_1=T_2\times T_2=A_1+E+T_1+T_2$; $T_1\times T_2=A_2+E+T_1+T_2$.

For T and T_h, drop subscripts 1 and 2 from A and T.

● RIASSUNTO (*)

Il fatto che sia emessa una prova definitiva con simulazione al computer classica per la correlazione statistica tra la rotazione molecolare e la traslazione porta ad una nuova valutazione della struttura quantistica dell'absorbimento rotazionale nelle microonde e nel lontano infrarosso. La correlazione classica implica che la teoria accettata di un absorbimento quantistico «rotazionale puro» sia solo una prima approssimazione. La traslazione di una molecola in alcuni ambienti influenza il proprio absorbimento quantizzato a causa della rotazione. Il numero di transizioni quantistiche permesse è aumentato dal valore teorico accettato $\Delta J=\pm 1$ a $\Delta J=\pm 1, \pm 2, \pm 3$ per tutte le molecole dipolari. Questi risultati sono ottenuti usando la teoria di gruppo che prevede anche che gli effetti della rotazione di traslazione aumentino il numero di transizioni permesse per ciascun numero quantico J e che quindi influenzino la distribuzione d'intensità delle linee di absorbimento. Questi risultati modificano fondamentalmente la teoria accettata della rotazione quantizzata. Teoricamente la distribuzione ben nota a $\Delta J=1$ è integrata da altre distribuzioni a $\Delta J=2$ e $\Delta J=3$.

(*) *Traduzione a cura della Redazione.*

Квантовая механика вращающихся и трансляционных молекул.
Часть I. - Полуклассическое рассмотрение.

Резюме (*). — С помощью классического компьютерного моделирования обнаружено подтверждение статистической корреляции между молекулярными вращением и трансляцией. Этот результат приводит к новой оценке квантовой структуры ротационного поглощения в микроволновой и далекой инфракрасной областях. Классическая корреляция подразумевает, что принятая теория «чистого

ротационного» квантового поглощения представляет только первое приближение. Трансляция молекулы в некоторой окружающей среде изменяет квантованное поглощение, вследствие вращения. Число разрешенных квантовых переходов увеличивается от теоретической величины $\Delta J = \pm 1$ до $\Delta J = \pm 1$, ± 2, ± 3 для всех дипольных молекул. Эти результаты получены, используя теорию групп, которая также предсказывает, что эффекты трансляции и вращения увеличивают число разрешенных переходов для каждого квантового числа J и, следовательно, изменяют распределение интенсивности для линий поглощения. Полученные результаты существенно видоизменяют принятую теорию квантованного вращения. Теоретически хорошо известное $\Delta J = 1$ распределение дополняется распределениями $\Delta J = 2$ и $\Delta J = 3$.

(*) *Переведено редакцией.*