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Report on Notation for the Spectra of Polyatomic Molecules*

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I. INTRODUCTION AND SUMMARY

A SATISFACTORY standardization of notation for diatomic molecules and their spectra already exists.[1] The problem of standardization for polyatomic molecules is much more complicated, because of the greater number of degrees of freedom for rotation and vibration, and because of the considerable variety of types of symmetry, or *symmetry groups*, to which polyatomic molecules belong, as contrasted with only two types ($C_{\infty v}$ and $D_{\infty h}$) for diatomic molecules. Fortunately, the system used in Herzberg's well-known book on infrared and Raman spectra[2] is already very generally accepted, and forms a suitable basis for the standard notation proposed here. However, when one considers the entire range of polyatomic spectroscopy, from ultraviolet to microwave and magnetic resonance spectra, there are several points of notation which need clarification, revision, supplementation, or simply codification and affirmation in a form to which spectroscopists of all wavelengths can conveniently refer. The principal need for supplementation, as compared with Herzberg's book, arises from the consideration of molecules in nontotally-symmetric electronic states, a matter which is especially essential for electronic spectra.

In some points the problem of notation for polyatomic spectra overlaps that for other related areas; in particular, valence theory, and the states of atoms in crystals. Some consideration has been given in this report to the needs of these areas, and a few recommendations have been made.

The problems are rather different for small molecules, the high symmetry of which is often very important for the classification of vibration modes and quantized states, and large molecules, where rigorous symmetry is often nonexistent or unimportant (though approximate or local symmetry is often important). Some consideration has been given in this report to large molecules, but the major emphasis is on the smaller or more symmetrical molecules.

This report in draft form has been sent to some 150 molecular spectroscopists and persons in allied fields for their criticism, comments, and suggestions, and the replies (from some 65 persons) have been very helpful in arriving at an end result which is believed to be acceptable in nearly all respects to almost all those who were consulted.

The conclusions reached are summarized in Table I, while the background for these conclusions, and certain further considerations, are presented in the subsequent text.

Where it is believed that existing practice is sufficiently well established, fairly unanimous, and ripe for current standardization, the conclusions are embodied in *Recommendations*. In a few cases where standardization would be premature or where the need for it is less definite, *Suggestions* have been made.

In some cases, more than one alternative notation has been included in a Recommendation, or it has been recommended that a particular notation be usually used, but that alternatives be not excluded under special circumstances. However, the acceptance of more than one alternative standard notation has never been recommended unless the alternatives are so different in form that there is no danger of their leading to confusion.

In this Report, pending a final decision by the Joint Commission,[3] the symbol cm^{-1} rather than K, and ν rather than σ for wave number, have been used. Further, as a matter of convenience to microwave spectroscopists, the symbol ν as well as related term symbols and molecular constants are permitted to signify quantities which may be expressed either in the usual cm^{-1} units, or in frequency (Mc/sec) units.

At all stages in the preparation of this Report, the writer has consulted extensively with Dr. G. Herzberg, whose cooperation and criticism have been of extremely great value, and who is in essential agreement with all the Recommendations, including those few which involve departures from notation of reference 2.

II. VIBRATIONAL AND ELECTRONIC STATES

1. Classification According to Symmetry Species

(a) *General Considerations*

The notation problem is in many respects very similar for vibrational and for electronic motions in molecules, hence it is convenient to treat these together. The major problem is to select definitions and symbols for the various symmetry-characterized types or "species" of classical normal modes of vibration and of

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[1] F. A. Jenkins, J. Opt. Soc. Am. 43, 425 (1953).

[2] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945). Other authors have given tables differing slightly in a few of the species symbols or definitions from those in Herzberg's book.

[3] See Minutes of Lund meeting, J. Opt. Soc. Am.

TABLE I. Summary and index of symbols and definitions.

Symbols or other items	Explanation	Reference
	(1) Quantum Numbers	
$\lambda, \sigma, \omega, \Lambda, \Sigma, \Omega; S$	Electronic quantum numbers for linear molecules, the same as for diatomic molecules (reference 1); resultant angular momentum of electron spins.	Rec. 2b
$v_i (i=1, 2, \cdots)$	Vibrational quantum numbers.	Rec. 8
v_2^+, v_2^- (e.g. $0^+, 0^-, 1^+, \cdots$)	Vibrational quantum numbers with superscripts to indicate inversion doubling components.	Rec. 11
$l_i, v_i^{l_i}, l$	Absolute value of vibrational angular momentum for degenerate vibrations of linear molecules; l_i for vibration with quantum number v_i, l for resultant angular momentum from all vibrations.	Recs. 9, 10
l_i	Angular momentum index for degenerate vibrations of symmetric-rotor molecules.	Rec. 9
J	Resultant angular momentum excluding nuclear spins.	Recs. 20, 25, 26
N	Resultant angular momentum excluding electron and nuclear spins, for the case that electron spin is present but loosely coupled.	Rec. 25
M, M_N, M_S	Projection of vector J, N, or S, respectively, on axis of axially symmetrical external electric or magnetic field.	Rec. 27
K	Absolute value of total angular momentum along axis of symmetric (or quasi-symmetric) rotor, exclusive of electron spin if present. For linear molecules, K is absolute value of vibronic (i.e., electronic × vibrational state) angular momentum for the case of electron spin zero or loosely coupled.	Rec. 21; Secs. III 2(b), (c), (d)
Σ	Component of vector S along axis of linear molecule or symmetric or quasi-symmetric rotor, if tightly coupled to vector K. The sign of Σ is positive or negative according as the component of vector S has the same or the opposite direction to K.	Rec. 26
P	Absolute value of total angular momentum along symmetry axis when vector S is tightly coupled to the latter. For linear molecules, $P=\lvert\pm\Lambda\pm l\rvert$. For symmetric (or quasi-symmetric) rotors, $P=\lvert K+\Sigma\rvert$.	Recs. 18, 26
(J,K)	Symbol for quantized rotational levels of symmetric-rotor molecules.	Rec. 21
$J_{K_aK_c}$ or J_τ	Symbols for quantized rotational levels of asymmetric-rotor molecules.	Rec. 22
I (or I_i)	Angular momentum of nuclear spin for one nucleus.	Rec. 28
T (or T_i)	Resultant angular momentum of nuclear spins for a set of like nuclei.	Rec. 28
F	Resultant angular momentum including everything.	Rec. 28
M_F, M_I, M_J	Projection of F, I, or J, respectively, on axis of axially symmetrical external electric or magnetic field.	Rec. 28
	(2) Electronic and Vibronic States	
General Considerations on Electronic States		Recs. 1, 14; Secs. II 1(a), II 3(a), (c)
General Considerations on Vibronic States		Sec. II 1(a), II 4
T_e	Electronic term (in cm^{-1} or Mc/sec).	Rec. 29
e, ev, v (as left superscript)	To distinguish electronic (^{e}) and vibronic (^{ev}), and vibrational (^{v}) states, *if necessary*.	Sug. 1
g, u (as subscripts)	Parity species symbols for orbitals and electronic and vibronic states of molecules *having a symmetry center* (g, u, denote symmetric or antisymmetric, respectively, on inversion at the center).	Recs. 2, 3
$^m\Sigma^+, {}^m\Sigma^-, {}^m\Pi, {}^m\Delta, \cdots$	Species symbols for electronic or vibronic states of unsymmetrical linear molecules ($m=2S+1=$ spin multiplicity), the same as for diatomic molecules (reference 1).	Rec. 2, Table II, and Sec. II 1(b)
$^m\Sigma_g^+, {}^m\Sigma_u^+, {}^m\Sigma_g^-, {}^3\Pi_u$, etc.	Species symbols for electronic or vibronic states of symmetrical linear molecules, the same as for diatomic molecules (reference 1).	Rec. 2, Table II, and Sec. II 1(b)
$^3\Pi_1, {}^2\Delta_{5/2}, {}^2\Pi_{(3/2)u}$, etc.	Linear-molecule electronic state symbols including subscripts for multiplet components, needed if spin is strongly coupled to molecular axis; the numerical subscript is the value of $\Lambda+\Sigma$, the same as for diatomic molecules (reference 1).	Rec. 2, and Sec. II 1(b)
$^mA, {}^mB, {}^mE, {}^mF$ or ^mT, usually with right subscripts or superscripts of one or more kinds	Species symbols for electronic or vibronic states of nonlinear molecules ($m=2S+1$); also for *atoms in crystals*. See SPECIAL RULES for B_i species (below).	Recs. 1, 3; Rec. 16

TABLE I.—*Continued.*

Symbols or other items	Explanation	Reference
B_i, often with further subscripts or superscripts	SPECIAL RULES are being recommended for labelling axes or planes in PLANAR and some other molecules in order to fix the uncertain meaning of the numerical subscript i in B_i and b_i species labels.	Recs. 4, 5a–d, Fig. 1
N, T, V, Q, V_i, ${}^3Q_u$, ${}^3L_a$, ${}^1L_b$, etc.	Informal symbols for special electronic states.	Rec. 15
(3) Orbitals and Electron Configurations		
General Considerations		Sec. II 3(b), (c)
g, u (as subscripts)	See under "(2) Electronic and Vibronic States."	
orbital	One-electron orbital wave function.	Rec. 12
spinorbital	One-electron wave function.	Rec. 12
AO, MO	Atomic orbital, molecular orbital.	Rec. 12
GO, SO, ASO, MSO	Group orbital, spin orbital, atomic spin orbital, molecular spin orbital.	Sug. 5
LCAO or LCAO-MO	MO approximated by a linear combination of AO*s*.	Sug. 5
$\sigma, \pi, \delta, \cdots$	Species symbols for MO*s* in linear molecules; also, for bond AO*s* of atoms in molecules; also, for bond MO*s*.	Recs. 2, 2a, Table I; Sug. 5
a, b, e, f or t, usually with subscripts or superscripts	Species symbols for MO*s* or GO*s* of nonlinear molecules; also, for AO*s* of atoms in crystals or molecules. For b_i species, see B_i above, under "(2) Electronic and Vibronic States," for SPECIAL RULES.	Recs. 3, 16
Electron Configurations and Numbering of MO*s*		Rec. 13, and what follows it
(4) Vibrational States		
General Considerations		Rec. 1
v (as left superscript)	To distinguish vibrational from electronic or vibronic states, *if necessary.*	Sug. 1
ζ_i	Coefficient of l_i in vibrational angular momentum of ith degenerate vibration.	Rec. 19a.
$G(v_1,v_2,\cdots)$	Vibrational term (in cm^{-1} or Mc/sec).	Recs. 29, 30
$\Delta_1 G(v_i)$, $\Delta_m G(v_i)$	Vibrational term differences, in particular $\Delta G(v_i) = G(v_1v_2, \cdots v_i+1, \cdots v_n) - G(v_1v_2\cdots v_i\cdots v_n).$	Rec. 33
ω_i, x_{ik}, $\cdots$	Coefficients in power series expression for vibrational term: $G=\Sigma_i\,\omega_i(v_i+\frac{1}{2}d_i) +\Sigma_i\,\Sigma_{k\geq i}\,x_{ik}(v_i+\frac{1}{2}d_i) \times(v_k+\frac{1}{2}d_k)+\cdots.$ Note that the definitions of ω and x here are different than for diatomic molecules,[1] where $G=\omega_e(v+\frac{1}{2}) -x\omega_e(v+\frac{1}{2})^2+\cdots.$	Rec. 30
ν_i	Symbol for ith vibration mode, also for wave number of corresponding fundamental band; for *numbering* of modes, see Rec. 6.	Rec. 6
σ, π, a, b, e, f, usually with subscripts or superscripts	Species symbols for vibration modes. For b_i species, see B_i under "(2) Electronic and Vibronic States," for SPECIAL RULES.	Recs. 1, 2a, Table II; Rec. 3
$\nu_3 b_{1u}$, $\nu_{16} e_g$, etc.	Combined numbering and species labeling of vibration modes.	Rec. 7
$\nu_1(\nu CH)a_g$, $\nu_3(\delta CH_2)a_g$, $\nu_4(\tau CH_2)a_u$, etc., $\nu(CCl)$, $\nu(\rho CCl)$	Examples of descriptive symbols for vibration modes which are fairly well localized.	Sugs. 2, 3
Σ^+, Σ^-, Π, Δ, $\cdots$ (or also with g, u subscripts)	Species symbols for vibrational states of linear molecules.	Recs. 1, 2, Table II, and Sec. II 1(b)
A, B, E, F, usually with subscripts or superscripts	Species symbols for vibrational states of nonlinear molecules. For B_i species, see B_i under "(2) Electronic and Vibronic States," for SPECIAL RULES.	Rec. 3
$(\nu_1 a_{1g})^2(\nu_6 b_{1u})^2 (\nu_{16} e_{2g})^2$, B_{1u} or $(\nu_1\sigma_g)^2(\nu_2\pi_u)^2 (\nu_3\sigma_u)$, Δ_u	Examples of vibrational configuration and state symbols.	Sug. 4
(5) Rotational and Over-all States		
General Considerations; Fine Structure		Secs. III 2(a), III 1
Eulerian Angles		Sec. III 1(a)
I_A, I_B, I_C or I^a, I^b, I^c, often with subscripts e, 0, or v_1, $v_2\cdots$	Principal moments of inertia, always with $I^c \geqslant I^b \geqslant I^a$. Subscript e denotes a true *equilibrium* value, subscripts v_1, v_2, $\cdots$ or 0 (for $v_1=v_2=\cdots=0$) indicate effective moments of inertia.	Rec. 19
A, B, C, usually with subscript e, 0, or v_1, $v_2\cdots$	Rotational constants (in cm^{-1} or Mc/sec), with e.g. (in cm^{-1}) $A_e=h/8\pi^2 c I_e{}^a$. Always $A\geqslant B\geqslant C$.	Rec. 19
$F(J)$, $F(J,K)$, $F(J_\tau)$, etc.	Rotational term (in cm^{-1} or Mc/sec) for linear or spherical-rotor molecule, symmetric-rotor, or asymmetric rotor, respectively.	Recs. 29, 31

TABLE I.—*Continued.*

Symbols or other items	Explanation	Reference
$F_1(J), F_2(J), \cdots$ $F_1(J,K), \cdots$	Term designations for components of fine structure levels due to loosely coupled electron spin. $F_1, F_2, \cdots$ refer to levels with $J=N+S, N+S-1, \cdots$.	Rec. 31, Part (2)
$F_a(J), F_b(J)$, $F_{1a}(J)$, etc.	Components of l-doublets or similar doublets; F_a and F_b are respectively the components of lower and higher energy.	Rec. 32
$F^{(+)}(J), F^{(0)}(J)$, $F^{(-)}(J)$	Term designations for Coriolis fine structure levels in 3-fold degenerate (F) vibrational states of spherical rotor molecules.	Rec. 32
$\Delta_1F(J), \Delta_2F(J)$, $\Delta_2F(J,K)$, $\Delta_2{}^KF(J,K)$, $\Delta_2F_{1a}(J)$, etc.	Rotational term differences, e.g. $\Delta_1F(J)=F(J+1)-F(J)$, $\Delta_2F(J,K)=F(J+1,K)-F(J-1,K)$, $\Delta_2{}^KF(J,K)=F(J,K+1)-F(J,K-1)$.	Rec. 33
$A_{[v]}, B_{[v]}$, $C_{[v]}, -D_{[v]}{}^J$, $-D_{[v]}{}^{JK}$ or $-D_{[v]}{}^{NK}, -D_{[v]}{}^K$ or $-D_{[v]}{}^N$	Rotational constants in power series expressions for $F(J,K)$ or $F_i(J,K)$ for linear or symmetric rotor molecule.	Rec. 31, parts (1)–(3)
$-\alpha_i, -\alpha_i{}^B, -\alpha_i{}^A$, $-\alpha_i{}^C$	Coefficients in power series expressions $B_{[v]}=B_e-\Sigma_i\alpha_i(v_i+\frac{1}{2}d_i)+\cdots$, etc.	Rec. 31, part (5)
A, A_1, A_2, B_1, B_2, B_3, E, F	Species symbols for rovibrational or rovibronic levels (i.e. over-all levels exclusive of hyperfine structure) of nonlinear molecules classified under rotational subgroup of vibrational symmetry group.	Rec. 23
s, a	Species symbols for classification of rovibrational or rovibronic levels of symmetrical linear molecules with respect to exchange of sets of identical nuclei.	Rec. 23
$+, -$	Parity species symbols for rovibronic levels (especially for linear and planar molecules).	Rec. 24
l- (or Λ-, Ω-, K-, or P-) doubling	Splitting of rovibronic levels into parity doublets.	Rec. 24 and the following
$++, +-, -+, --$; or A, B_c, B_a, B_b	Symbols for the four asymmetric-rotor rotational species.	Rec. 22
	(6) Spectroscopic Transitions	
$'\ ''$ (prime and double prime)	Used to distinguish the upper ($'$) and lower ($''$) levels in a spectroscopic transition. Examples: $F', G(v_1',v_2',\cdots), J'', B_{[v]}''$.	Rec. 34, Sec. IV 2(a)
$\Delta J, \Delta K, \Delta v_i$, etc.	ΔJ means $J'-J''$, $\Delta v_i=v_i'-v_i''$, etc.	Rec. 35
$-$ (minus sign or dash)	Placed between symbols of upper state (*always first*) and lower state, as symbol for a spectroscopic transition. Examples: ${}^3B_2-{}^1A_1$ electronic transition; (3,2)−(2,1) rotational line of symmetric rotor molecule.	Rec. 36
$\leftarrow, \rightarrow$	Used instead of $-$ sign if it is desired to indicate specifically an absorption transition $(T'\leftarrow T'')$ or an emission transition $(T'\rightarrow T'')$.	Rec. 36
$\nu_1+2\nu_2-\nu_3$, or the like	To indicate a band in the vibrational spectrum.	Rec. 37
ν_e	Electronic "frequency" or origin of a band system (in cm^{-1}); $\nu_e=T_e'-T_e''$.	Rec. 38
ν_0	Origin of a band (in cm^{-1}): $\nu_0=\nu_e+(G'-G'')$.	Rec. 38
band; (electronic) transition; band system		Rec. 39
O, P, Q, R, S	To denote band branches with ΔJ (or ΔK)$=-2, -1, 0, +1, +2$ respectively.	Rec. 40
${}^RQ(J)$, etc.	Band line with $\Delta K=1$, $\Delta J=0$, and a value of J'' equal to the J value given in parentheses; etc.	Rec. 40
${}^RQ_{12}(J)$, etc.	Like ${}^RQ(J)$, etc. but with loosely coupled electron spin S whose orientation is implicitly given by the numerical subscripts (first subscript for upper state, second for lower state); $J'=N'+S=J''=N''+S-1$ in example given.	Rec. 41
Use of R, S in rotational Raman spectra		Rec. 42

quantum-mechanical eigenfunctions. These species are best characterized by group-theoretical methods. For any molecule of given symmetry, each symmetry species is defined, and its species label assigned, to correspond to a characteristic behavior under each of the various "classes" of symmetry operations of the symmetry group.

The classification according to symmetry species is most important for small molecules of high symmetry. For molecules lacking any symmetry, no rigorous classification is possible, but partial or approximate classifications based on local or approximate symmetry are often useful.

The things which require classification fall into the five categories given just below. **It is recommended (REC. 1)** that, *for any given symmetry group*, identically the same set of species symbols be used for all five categories, except that *lower case letters* be used for categories (a) and (c), *capital letters* for (b), (d), and (e).

(a) *Normal vibration modes:* lower case letters.
(b) *Vibrational state wave functions:* capital letters.
(c) *Orbitals* (i.e., one-electron orbital electronic wavefunctions): lower case letters.
(d) *Electronic state wave functions:* capital letters.
(e) *Vibronic state* (i.e., combined electronic × vibrational state) *wave functions:* capital letters.

The use of the same capital-letter species symbols for categories (b), (d), and (e) will seldom cause confusion. The context will usually make clear which category is involved. However, **it is suggested** (**SUG. 1**) that, *if necessary* for clarity, the species symbols be prefixed by a left superscript ^{v}, ^{e}, or ^{ev} for a vibrational, electronic, or vibronic state respectively; for example, $^vE_{2g}$, $^{e3}B_1$, $^{ev2}A'$.

(*b*) *Linear Molecules*

Two systems of species symbols are in common use. One, using Greek letters, was first developed for orbitals and electronic states of diatomic molecules. Diatomic, and also *linear polyatomic*, molecules belong to symmetry groups $C_{\infty v}$ for unsymmetrical, $D_{\infty h}$ for centrosymmetric, molecules. Hence **it is recommended** (**REC. 2**), in agreement with general practice, that use of the diatomic electronic species symbols be extended to all of the five classification categories given above, for all *linear molecules*.

Table II and the subsequent discussion indicate the species symbols for molecules of symmetry $C_{\infty v}$. In categories (d) and (e), a left superscript to denote the spin multiplicity m is usually included, e.g., $^1\Sigma^+$, $^3\Pi$, and so on. Right subscripts to indicate multiplet components are also added if the spin if sufficiently strongly coupled to the symmetry axis (Hund's diatomic case *a*) e.g., $^3\Pi_1$, $^2\Delta_{5/2}$.[1] If the spin-orbit coupling is very strong (Mulliken's case *c*), other species symbols ($0^+, 0^-, 1, 2, \cdots$) related to the multiplet component subscripts of Hund's case *a* are used.[1]

In categories (a) and (c), not all of the species which otherwise exist are possible. The only σ species are σ^+, never σ^-. Hence **it is recommended** (**REC. 2a**) that the species symbol σ^+ be abbreviated to σ, as in Table II, in agreement with diatomic practice.[1]

For molecules of symmetry $D_{\infty h}$, there are *two* species corresponding to each *one* of Table II. These are distinguished by a right subscript *g* or *u*. For example, there are σ_g, σ_u, π_g, and π_u vibration modes, $\Sigma_g{}^+$, $\Sigma_g{}^-$, $\Sigma_u{}^+$, $\Sigma_u{}^-$, $\cdots$ vibrational states, electronic states such as $^2\Sigma_g{}^+$, $^2\Sigma_u{}^+$, $^4\Sigma_g{}^-$, $^3\Pi_{1u}$, $^2\Delta_{(5/2)g}$, and so on.

Table II. Species symbols for symmetry $C_{\infty v}$.

(a) Vibration modes:	σ,		π				
(b) Vibrational states:	Σ^+,	Σ^-,	Π,	Δ,	Φ,	Γ,	$\cdots$
(c) Orbitals:	σ,		π,	δ,	ϕ,	γ,	$\cdots$
(d) Electronic states:	$^m\Sigma^+$,	$^m\Sigma^-$,	$^m\Pi$,	$^m\Delta$,	$^m\Phi$,	$^m\Gamma$,	$\cdots$
(e) Vibronic states:	$^m\Sigma^+$,	$^m\Sigma^-$,	$^m\Pi$,	$^m\Delta$,	$^m\Phi$,	$^m\Gamma$,	$\cdots$

In addition to species symbols, quantum number symbols are needed. For categories (c) and (d), **it is recommended** (**REC. 2b**) that the same angular momentum quantum number symbols (in particular, λ_i, S, Λ, Σ, Ω) be used for *all linear molecules* as for diatomic molecules.[1] For categories (a) and (b), however, distinctive symbols (l_i and l instead of the analogous diatomic λ_i and Λ; also v_i) are recommended [see Sec. II2 (b), Recommendations 8–10]. Likewise for category (e), distinctive symbols for angular momentum quantum numbers are recommended (see Sec. II 4).

(*c*) *Nonlinear Molecules*

A second system of species symbols, using italic letters with subscripts and superscripts, was developed by Placzek for nonlinear molecules.[4] This was first used for vibrational modes and states, but was soon applied also to orbitals and electronic and vibronic states.[5] The most complete tabulations of the symbols and the group-theoretical specifications of the possible symmetry species, for all important molecular symmetry groups, are those given by Herzberg.[2] Herzberg uses the diatomic symbols for linear molecules, and the Placzek symbols with minor changes for nonlinear molecules.

It is recommended (**REC. 3**) that species symbols and their definitions precisely as given by Herzberg in Chapter II, Sec. 3, of his book[2] *be adopted as standard for nonlinear molecules*, for all the five categories of vibrational and electronic classification given above, with capital or lower case letters in accordance with Recommendation 1, and left superscripts to indicate multiplicity (in the same way as for linear molecules, see Table I) for electronic and vibronic states; but leaving open the possibility of using alternative symbols when particularly desirable in special situations; in particular, the symbols[5] T and t should be used instead of F and f for triply-degenerate states or orbitals of atoms in crystals [see Sec. II 3(d)].

Recommendations 1–3 still leave unsolved one troublesome problem which arises for symmetry species bearing labels B_i or b_i ($i=1$, 2, and sometimes also 3), or B_{ip} or b_{ip} ($p=g$ or u), for the symmetry groups C_{2v}, C_{4v}, C_{6v}, D_2, D_4, D_6, D_{2h}, D_{4h}, and D_{6h}. (No such difficulty arises for B species of other groups, nor for A, E, or F species of any group.) The difficulty is that the distinctions between B or b species differing in numerical subscript depend on their behavior toward certain pairs of classes of symmetry operations which, while group-theoretically distinct, cannot be distinguished by any general specification for the particular symmetry group, but only by a specification for a particular molecule or type of molecule. As a result, confusing divergences exist: for

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[4] G. Placzek, in Marx's *Handbuch der Radiologie* (Akademische Verlagsgesellschaft, Leipzig, Germany, 1934), Vol. VI, 2, p. 205; article on Raman spectra.

[5] R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

example, one author calls B_1 the same species which another calls B_2, and vice versa. There seems to be no *general* solution for this problem. Hence **it is recommended** (**REC. 4**) that in general every author, in referring to B_i or B_{ip} (or b_i or b_{ip}) species of the symmetry groups mentioned above, shall define these species clearly *in each paper* in terms of the specific geometry of the molecules he is discussing and in so doing, that he shall make an effort to follow previous usage if such exists and there is no strong reason to change.

However, for the very large and important class of *planar* molecules of symmetry groups C_{2v}, D_{2h}, D_{4h}, and D_{6h}, the need for an immediate standardization of B_i or b_i species labels is urgent. In defining the problem, it should be noted that *not all* molecules of the groups mentioned are planar; but also that planar molecules exist belonging to other symmetry groups (C_s,C_{ph},D_{3h},D_{5h}) for which no B_i problem exists either because there are no B species or (C_{ph}) because only B_g and B_u species occur.

The group-theoretical species table for C_{2v} is given in Table III. The species B_1 and B_2 are distinguished by their behavior for reflection in the two planes $\sigma_v(xz)$ and $\sigma_v(yz)$. The z-axis is the axis of symmetry, but the choice of the x- and y-axes, hence the identification of the two planes, is arbitrary, with two choices possible. To resolve the resulting ambiguity in the meaning of the B species labels, **it is recommended** (**REC. 5a**) that, for *planar* C_{2v} molecules, the x-axis always be chosen perpendicular to the plane of the molecule unless there are very exceptionally strong reasons for a different choice; and that the choice of axes used also be explicitly stated, as per REC. 4, even if it is the standard choice. Application of this rule to some typical examples is illustrated in the following Fig. 1.

The group-theoretical species table for D_{2h} is given in Table IV.[2] The species B_{1p}, B_{2p} and B_{3p} ($p=g$ or u) can most conveniently be characterized by their respective behaviors for 180° rotations around the three mutually perpendicular 2-fold principal axes of symmetry z, y, and x. However, the assignment of the labels z, y, and x to the three axes in a particular molecule is arbitrary, with six choices possible. To resolve the resulting ambiguity in assigning B species labels, **it is recommended** (**REC. 5b**) that, for *planar* D_{2h} molecules, the x axis be chosen perpendicular to the plane of the molecule and the z-axis so that it passes through the greatest number of atoms or, if this rule is not decisive, so that it cuts the greatest number of bonds; these rules are to be followed unless there are very exceptionally strong reasons for a different choice; and that the choice of axes used also be explicitly stated, as per REC. 4, even if it is the standard choice. Application of REC. 5b to some typical examples is illustrated in Fig. 1.

TABLE III. Species table for symmetry C_{2v}.

C_{2v}	I	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	+1	+1	+1	+1
A_2	+1	+1	−1	−1
B_1	+1	−1	+1	−1
B_2	+1	−1	−1	+1

TABLE IV. Species table for symmetry D_{2h}.

D_{2h}	I	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	i	$C_2(z)$	$C_2(y)$	$C_2(x)$
A_g	+1	+1	+1	+1	+1	+1	+1	+1
A_u	+1	−1	−1	−1	−1	+1	+1	+1
B_{1g}	+1	+1	−1	−1	+1	+1	−1	−1
B_{1u}	+1	−1	+1	+1	−1	+1	−1	−1
B_{2g}	+1	−1	+1	−1	+1	−1	+1	−1
B_{2u}	+1	+1	−1	+1	−1	−1	+1	−1
B_{3g}	+1	−1	−1	+1	+1	−1	−1	+1
B_{3u}	+1	+1	+1	−1	−1	−1	−1	+1

The group-theoretical tables for D_{4h} and D_{6h} molecules (Herzberg[2]) read in part as in Tables V and VI. (It may

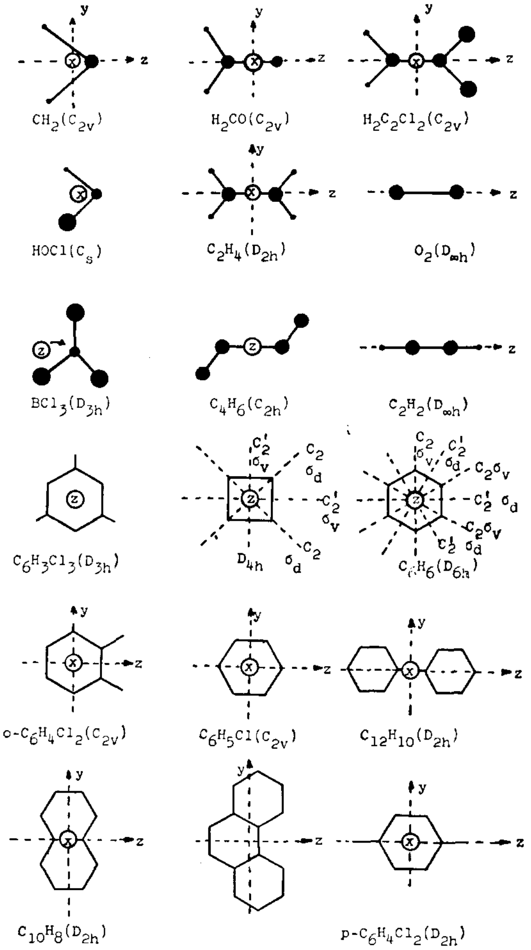

FIG. 1. Recommended axis choices for planar molecules. In every case z is the (or for D_{2h}) a principal axis of symmetry. The choices of the x- and y-axes (and of z for D_{2h}) are then free, *except* that for C_{2v} and D_{2h} molecules they must be fixed if the B species labels are to be made unambiguous. For D_{4h} and D_{6h} molecules, the labeling of the C_2 and C_2' sets of axes (but *not* of the x- and y-axes) must similarly be fixed to make the B species labels unambiguous. The circle around x or z in each diagram indicates a downward direction into the plane of the paper.

TABLE V.

D_{4h}	I	$\cdots$	$2C_2$	$2C_2'$	$2\sigma_v$	$2\sigma_d$
B_{1g}	$+1$	$\cdots$	$+1$	-1	$+1$	-1
B_{1u}	$+1$		$+1$	-1	-1	$+1$
B_{2g}	$+1$		-1	$+1$	-1	$+1$
B_{2u}	$+1$		-1	$+1$	$+1$	-1

TABLE VI.

D_{6h}	I	$\cdots$	$3C_2$	$3C_2'$	$3\sigma_v$	$3\sigma_d$
B_{1g}	$+1$	$\cdots$	$+1$	-1	-1	$+1$
B_{1u}	$+1$		$+1$	-1	$+1$	-1
B_{2g}	$+1$		-1	$+1$	$+1$	-1
B_{2u}	$+1$		-1	$+1$	-1	$+1$

be noted that the tables contain implicit definitions of the operations σ_v and σ_d in terms of C_2 and C_2', as follows: for D_{4h}, $\sigma_v = iC_2'$, $\sigma_d = iC_2$; for D_{6h}, $\sigma_v = iC_2$, $\sigma_d = iC_2'$ (i is the inversion operation). **It is recommended (REC. 5c)** that the following rule, which in the most important cases is in agreement with the current practice of most authors, be adopted for *planar* D_{4h} and D_{6h} molecules in order to make the designations of their B_{1p} and B_{2p} species unambiguous: the C_2 and C_2' classes of operations in the tables shall be distinguished by specifying that, (a), the C_2 axes shall pass through the greater numbers of atoms or, (b), in case specification (a) is not decisive, shall intersect the greater numbers of bonds. Application of this rule to some examples is illustrated in Fig. 1.

A similar standardization of B species labels appears desirable for those C_{4v} and C_{6v} molecules which, while not planar, nonetheless contain a square or hexagonal planar arrangement of atoms. The group-theoretical tables[2] here read in part as follows:

C_{4v}	$\cdots$	$2\sigma_v$	$2\sigma_d$	C_{6v}	$\cdots$	$3\sigma_v$	$3\sigma_d$
B_1		$+1$	-1	B_1		$+1$	-1
B_2		-1	$+1$	B_2		-1	$+1$

Here **it is recommended (REC. 5d)** that the σ_v and σ_d classes of operations be distinguished by the specification that, (a), the σ_v planes shall pass through the greater number of those atoms which are in the square or hexagonal (or similar) array, or, (b), in case specification (a) is not decisive, shall intersect the greater number of bonds among such atoms. The locations of the σ_v planes are thus similar to those of the C_2 axes in the D_{4h} and D_{6h} cases in Fig. 1.

It will be noted that the foregoing recommendations 5a–5d do not resolve ambiguities as to B species labels for molecules of groups D_2, D_4, or D_6, nor for *nonplanar* molecules of groups C_{2v}, D_{2h}, D_{4h}, or D_{6h}. For these cases, it appears best merely to follow REC. 4.

A few comments are needed on the changes required in current practice by RECS. 5a and 5b. At the present time, most workers on electronic structure and spectra[5] are already in accord with these recommendations; but most workers on infrared and Raman spectra[2] use a notation corresponding to an interchange of the x and y axes as compared with REC. 5a for C_{2v} molecules and of the x- and z-axes as compared with REC. 5b for D_{2h} molecules. The infrared workers must then interchange their x- and y-axis labels and their B_1 and B_2 species labels if they are to follow REC. 5a. They may also have to change the present numbering of some of the vibration modes of some C_{2v} molecules (not, however, for a B_2 molecules) if they also follow REC. 6 below. For D_{2h} molecules they must interchange their present x and z axis labels and consequently (see Table IV) their B_{1p} and B_{3p} species labels ($p = g$ or u) if they are to follow REC. 5b.

RECS. 5a and 5b have the advantage that planar molecules of symmetries C_{2v} and D_{2h}, and related linear molecules, usually have the z axis in a convenient and natural direction (see Fig. 1), and the x-axis perpendicular to the molecule plane (and/or to the principal axis). It may be noted that **RECS. 5a** and **5b** have the endorsement of Dr. G. Herzberg.

2. Normal Vibration Modes and Vibrational State Wave Functions

(a) *Vibration Modes*

The *labeling* of *normal modes of vibration* according to group-theoretical species has been covered in RECS. 1–5d (also, see Table II and Fig. 1). Further, **it is recommended (REC. 6)** that the vibration modes of any molecule be labeled and *numbered* in the way described at the top of p. 272 of Herzberg's book,[2] beginning the numbering with ν_1 for the highest frequency totally symmetric mode; but following Herzberg also in designating the perpendicular vibration of linear XY_2 and XYZ molecules, as a single exception to the usual rule, always by ν_2; it is to be understood that these symbols are not only labels for vibration modes but also symbols for the wave number values, of the corresponding fundamental bands (see Sec. IV); further, the parallel use for special purposes (for example, comparisons between isotopic molecules) of other modes of numbering normal modes of vibration should not be entirely excluded.

For a more complete description of any vibration mode, **it is recommended (REC. 7)** that the species symbol be added, for example $\nu_{16}e_{2g}$.

In case it is known that the motion in a particular mode is largely localized in a particular bond or a particular group or groups of atoms, **it is suggested (SUG. 2)** that further descriptive symbols be included, for example $\nu_1(\nu CH)a_g$; $\nu_2(\nu C{=}C)a_g$; $\nu_3(\delta CH_2)a_g$; $\nu_4(\tau CH_2)a_u$; $\nu_5(\nu CH)b_{1g}$; $\nu_6(\rho CH_2)b_{1g}$; $\nu_7(\omega CH_2)b_{3u}$; $\nu_8(\omega CH_2)b_{2g}$ for some of the normal modes of C_2H_4 (ν = stretching, δ = deformation or spreading, τ = twisting, ω = wagging, ρ = rocking). The use of symbols such as ν, δ, ρ, τ, ω should be avoided except when it is known that they represent reasonable approximations to the actual motions. For semilocalized vibrations of *large molecules* or molecules of *low symmetry* where the vibration modes have not been identified and numbered in terms of symmetry species, **it is suggested** (**SUG. 3**) that, when warranted, symbols such as $\nu(CCl)$, $\nu(\rho CCl)$, $\nu(\omega CCl)$ be used.

(*b*) *Quantum Numbers and Vibrational State Wave Functions*

It is recommended (**REC. 8**) that the vibrational quantum number for the ith vibrational mode be designated by v_i.

In the special case of degenerate vibrations of linear and symmetric-rotor molecules, a second quantum number or index besides v_i is needed; **it is recommended** (**REC. 9**) that this be designated l_i and that particular values of the pair v_i, l_i be written in the form $v_i^{l_i}$ for example $v_2^{l_2}=2^2$ or 3^1; in linear molecules, l_i is vibrational angular momentum around the molecular axis in units of $h/2\pi$. In symmetric-rotor molecules, l_i gains significance only for rovibrational states where there is rotation ($K>0$) around the molecular axis; for each degenerate vibration there is then a vibrational angular momentum $(\pm\zeta_i l_i)h/2\pi$, the sign depending on whether l_i is parallel ("$+l_i$") or antiparallel ("$-l_i$") to K; the use of the symbol ζ_i **is recommended** (**REC. 9a**) for the purpose indicated here. There is an energy splitting between the $+l_i$ and $-l_i$ states: see Sec. IV, REC. 31, part (1), also Sec. III 2(b).

The labeling of over-all vibrational state wave functions has been covered in RECS. 1–5d. In the case of linear molecules, a quantum number label for the resultant vibrational angular momentum quantum number (vector Σl_i) around the figure axis is also needed, and **it is recommended** (**REC. 10**) that l be used for this purpose [$l=0, 1, 2, \cdots$ for Σ^+ or Σ^-, Π, Δ, $\cdots$ states (see Table II)].

For more detailed characterization of vibrational states, **it is suggested** (**SUG. 4**) that *vibrational configuration symbols* be combined with state symbols as in the following examples:

$$(\nu_1)^2\nu_6(\nu_{16})^2,\ B_{1u} \quad \text{or} \quad (\nu_1a_{1g})^2(\nu_6b_{1u})(\nu_{16}e_{2g})^2,\ B_{1u}$$
$$(\nu_1)^2(\nu_2)^2\nu_3,\ \Delta_u \quad \text{or} \quad (\nu_1\sigma_g)^2(\nu_2\pi_u)^2(\nu_3\sigma_u),\ \Delta_u$$

for a nonlinear and a linear molecule, respectively.

In cases, such as NH_3, where *inversion doubling* of vibrational levels occurs, designations for the two sublevels are needed. Herzberg (reference 2, pp. 222, 295), uses superscripts + and − (e.g., 0^+, 0^-, 1^+, 1^-, $\cdots$ for $v_2=0, 1, \cdots$ in the case of NH_3). **It is recommended** (**REC. 11**) that these be used.

3. Electron Configurations and Electronic States

(*a*) *General Considerations on the Classification of Electronic Wave Functions*

(1) It is important to keep in mind that the group-theoretical species classification of electronic wave functions of molecules is based on the symmetry of the geometrical configuration of the nuclear framework, ordinarily for an idealized situation in which the nuclei are thought of as held fixed in positions corresponding to equilibrium for the particular electronic state under consideration. Unlike the symmetry for vibrational modes and states, the equilibrium molecular symmetry for an electronic state is practically unaffected by isotopic substitution; hence the appropriate electronic state species classification is the same for all isotopic molecules. For example, the ground state of CO_2 is classified as $^1\Sigma_g^+$ ($D_{\infty h}$ symmetry) equally for $O^{16}C^{12}O^{16}$, $O^{16}C^{12}O^{18}$, and other isotopes. The spectroscopic properties of an electronic state (i.e., the selection rules and over-all intensities of transitions to other electronic states) are to a good approximation governed by this fact. However, in a higher order of approximation, the classification can also be given in terms of that lower symmetry which is appropriate in classifying the vibrational states; for example the ground state of $O^{16}C^{12}O^{18}$ may be classified as $^1\Sigma^+$ (symmetry $C_{\infty v}$).

(2) When substituent groups are introduced into a molecule, the major spectroscopic properties, at least for some electronic transitions, are often little affected, in spite of the fact that the rigorous symmetry classifications of the states involved may be changed. For example, all unconjugated aldehydes RCHO and ketones R_2CO show a characteristic weak ultraviolet absorption band system near λ2900, indicating that all have a very similar excited electronic state, and that to a rather good approximation all behave as if they had symmetry C_{2v} like H_2CO. The situation is similar to that for isotopic substitution, although the effects of substitution are in general greater. For this reason, classification according to approximate or local symmetry is more frequently useful for electronic than for vibrational states.

(3) Different electronic states of a molecule in general differ in their nuclear equilibrium configurations, in respect to (a) interatomic distances; (b) often also symmetry. When situation (b) occurs, the species classification must be made in terms of different symmetry groups for different states. Nevertheless, because of the operation of the Franck-Condon principle, the electronic selection rules and the over-all intensity of the system of bands (and/or continuum) associated with an electronic transition always correspond in first approximation to those for a transition without change of symmetry, in other words to those for a transition keeping the symmetry of the *initial state* (whether in absorption or in emission). Hence classification of the final state wave function according to the initial state symmetry is often desirable.

For a detailed consideration of individual bands and band-lines, however, one must use electronic (and/or vibronic) selection rules corresponding to a sort of *greatest common denominator* of the symmetries of the initial and final equilibrium configurations.

In assessing the likelihood that situation (b) may occur, it is important to keep in mind the Jahn-Teller theorem,[6] which states that orbitally-degenerate (i.e., E or F) states of *nonlinear* molecules are configurationally unstable. However, no quantitative studies of the Jahn-Teller effect have been made, and it is possible that in many cases only a small or moderate departure from a geometrical configuration of the original symmetry may occur. On the other hand, changes of symmetry on going to excited states are frequent even for orbitally nondegenerate states and for linear molecules.

(4) Among large aromatic molecules there are often extensive close analogies between the ultraviolet spectra of molecules which would not on any obvious grounds be expected to be spectroscopically related.[7] Here an empirical classification of electronic states becomes more useful than one based on symmetry species.

(*b*) *General Considerations on the Labeling of Orbitals in Molecules and Crystals*

The labeling of one-electron wave functions of molecules,[8,9] and of atoms in crystals, is a problem common to valence theory and to spectroscopy. As a preliminary to the discussion, **it is recommended** (**REC. 12**) that the word "orbital" be used only to mean "one-electron orbital wave function;"[9(a)] further, that the words "*atomic orbital*" (which may be abbreviated AO) and "*molecular orbital*" (which may be abbreviated MO) be used to refer to one-center and two-or-more center orbitals, respectively; further, that "spin orbital" be used to mean a one-electron wave function which is a product of an "orbital" times a one-electron spin function.[9b] Further, **it is suggested** (**SUG. 5**) that, in polyatomic molecules, MO*s* belonging to a pair of linked atoms, and to the molecule as a whole, be respectively called *bond* MO*s* (or BMO*s*), *group* orbitals (or GO*s*), and *nonlocalized* or *whole-molecule* MO*s*; BMO*s* and GO*s* are respectively localized and semilocalized MO*s*; when MO*s* of any kind are approximated as linear combinations of atomic orbitals, they may be called LCAO-MO*s*, or LCAO*s*; spinorbitals (or SO*s*) include "atomic spinorbitals" (ASO*s*) and "molecular spinorbitals" (MSO*s*).

In molecular spectroscopy, whole-molecule MO*s* are usually the most convenient orbitals to use. It should be noted, however, that automatic localization often occurs so that some whole-molecule MO*s* take the form, to a more or less good approximation, of GO*s* or even AO*s*. In valence theory, whole-molecule MO*s*, GO*s*, BO*s*, and variously-selected AO*s* (including both proper AO*s* and "hybrid" AO*s*), are all useful for various purposes. For atoms in crystals, variously-selected AO*s* are used.

When AO*s* are used for atoms in molecules, the viewpoint is essentially the same as for atoms in crystals, namely that the AO*s* used are selected and classified to conform to the symmetry of the *local field* set up by the action of neighboring atoms. In both cases, one may often classify the AO*s* according to a *dominant* but approximate symmetry, corresponding, perhaps, to the local fields of next-neighbor atoms only, or according to an (often lower) *rigorous* symmetry corresponding to the fields of all sufficiently near atoms. Classifications according to both dominant and rigorous symmetry are important for the spectroscopy of atoms in crystals. Molecules or molecular ions in crystals are subject to similar considerations.

(*c*) *Electron Configurations and Electronic States of Molecules Using Whole-Molecule Orbitals*

The labeling of MO*s* and of electronic state wave functions according to group-theoretical species has already been dealt with in RECS. 1–5d (see also Table II and Fig. 1).

For the designation of electron configurations together with electronic states in spectroscopy, **it is recommended** (**REC. 13**) that, ordinarily, whole-molecule MO*s* be used and that, *within each group-theoretical species*, these be numbered consecutively, beginning with 1 for the most firmly bound MO of the given species; however, when more convenient, inner-shell orbitals may be assigned to AO*s* of the separate atoms, and the numbering of the MO*s* begun with the valence-shell MO*s*. Following are some examples, for the ground states of several molecules.

$$\mathrm{CO_2}\text{: } (1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (3\sigma_g)^2\ (2\sigma_u)^2\ (4\sigma_g)^2\ (3\sigma_u)^2\ (1\pi_u)^4\ (1\pi_g)^4,\ {}^1\Sigma_g{}^+\ (D_{\infty h});$$

or

$$(1s_O)^2\ (1s_O)^2\ (1s_C)^2\ (1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (1\pi_g)^4,\ {}^1\Sigma_g{}^+\ (D_{\infty h}).$$

$$\mathrm{CH_4}\text{: } (1a_1)^2\ (2a_1)^2\ (1f_2)^6,\ {}^1A_1\ (T_d).$$

$$\mathrm{H_2CO}\text{: } (1a_1)^2\ (2a_1)^2\ (3a_1)^2\ (4a_1)^2\ (1b_2)^2\ (5a_1)^2\ (1b_1)^2\ (2b_2)^2,\ {}^1A_1\ (C_{2v}).$$

$$\mathrm{CrO_4{}^=}\text{: } (1a_1)^2\ (1f_2)^6\ (1e)^4\ (2f_2)^6\ (2a_1)^2\ (3f_2)^6\ (1f_1)^6,\ {}^1A_1\ (T_d).$$

The electron configurations of molecules are formally (but only formally) closely similar to vibrational configurations [see Sec. II 2(b)]. Just as in the case of vibrational modes [see Sec. II 2(a)], the standard brief orbital symbols in an electron configuration may, *when warranted*, be supplemented by the addition of further symbols giving approximate descriptions of the detailed forms of the MO*s*; symbols more or less similar to those used for this purpose for diatomic molecules[1] are appropriate.

In case there can be any doubt [see Sec. IV 3(a), item (3)] as to the symmetry which is being assumed for a molecule in a particular electronic state, **it is recommended** (**REC. 14**) that the symbol for the sym-

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[6] See, for example, H. Sponer and E. Teller, Revs. Modern Phys. **13**, 75 (1941).

[7] See J. R. Platt, J. Chem. Phys. **17**, 484 (1949); **19**, 101, 1418 (1951).

[8] F. Hund, Z. Physik **73**, 1 (1932).

[9] R. S. Mulliken, (a) Phys. Rev. **41**, 50 (1932); (b) J. chim. phys. **46**, 502 (1949).

metry group be added in parentheses after the state species symbol, as in the examples given above. This procedure is especially useful when there is a change of symmetry upon electronic excitation. For example, CO_2 is linear in its ground state, but nonlinear in its first singlet excited state. It has been suggested that the latter corresponds to a $^1\Pi_g$ state of a linear molecule,[10] but that this is split into a $^1A_2(C_{2v})$ and a $^1B_2(C_{2v})$ state, with the observed absorption bands going to the $^1B_2$ state. The electronic transition might then be described as

$$^1B_2(C_{2v})-{}^1\Sigma_g{}^+(D_{\infty h}).$$

For brief reference, **it is recommended (REC. 15)** that, in agreement with common practice, various simple letter symbols be used (with or without species symbol) to identify particular electronic states. For example, N may be used for the ground state, E, T, V, Q, ^3Q_u, V_i, ^3L_a, ^1L_a, ^3L_b, for various types of excited states, but a definite standardization of these letter symbols does not seem necessary at present.

(*d*) *Orbitals and States of Atoms in Crystals*

For atoms in crystals, if the crystalline fields are strong enough to break down the original spin-orbit couplings, exactly the same electronic state species symbols as for molecules are suitable, and **it is recommended (REC. 16)** that they be used, except that the molecular symbols F and f be replaced by T and t (see REC. 3), in order to avoid confusion with the atomic species symbols F and f. For example, an atom in a $^3D^\circ$ state, when subjected to a strong enough crystalline field of symmetry O_h, gives rise to a ^3E_u and a $^3T_{2u}$ state; if to a strong enough field of symmetry C_{2v}, to one $^3A_1$, two $^3A_2$, one $^3B_1$, and one $^3B_2$ states.[5]

This nomenclature, however, does not provide for the classification of weak-field states, or of multiplet components, except in the unlikely case of a perturbing field with symmetry $C_{\infty v}$ or $D_{\infty h}$, where the diatomic nomenclature surveyed in Sec. II 1(b) is appropriate. In other cases, resort must be had, for the time being, to the relatively uninformative notation introduced by Bethe.[11] A suitable extension of the Placzek notation is needed here.

In very strong crystalline fields, a classification not only of the states, but also of the AO*s* of the outer electrons according to crystalline-field species is needed. For example, in a strong enough O_h field a $3d$ AO gives rise to an e_g (twofold degenerate) and a t_{2g} (threefold degenerate) AO; or in a C_{2v} field to an a_1, two a_2, a b_1, and a b_2 AO. For a complete description, one may speak here of $3de_g$ and $3dt_{2g}$, or of $3da_1$, $3da_2$, $3db_1$, and $3db_2$ AO*s*. Perhaps these crystalline-field AO*s* might be designated as CAO*s*.

4. Vibronic States

The labeling of vibronic (i.e., electronic × vibrational) state wave functions has been covered in RECS. 1–5d. One special point should be noted: the species classification for any vibronic state is to be based on the symmetry group appropriate for the vibrational and not for the electronic state involved, in case these differ, as for example because of isotopic substitution [see Sec. II 3(a)].

For the vibronic states of *linear molecules*,[12,13] certain special angular momentum quantum numbers are sometimes needed. In general, one may have an electronic resultant orbital angular momentum quantum number Λ ($\Lambda=|\text{sum of } \pm\lambda_i\text{'s}|$), just as for diatomic molecules,[1] and a vibrational resultant orbital angular momentum quantum number l ($l=|\text{sum of } \pm l_i\text{'s}|$), see REC. 10.

There are now two cases, depending on how strongly the electronic spin S is coupled to the molecular axis by the magnetic field corresponding to Λ (and/or, possibly, to l). If $S=0$, or if with $S>0$ the spin is loosely coupled, Λ and l form a resultant, and **it is recommended (REC. 17)** that this be called K; $|\pm\Lambda\pm l|=K$; if $\Lambda=0$ (the usual case for infrared and Raman spectra), $l\equiv K$, but the notation l is usually to be preferred, while if $l=0$, $\Lambda\equiv K$, but the notation Λ is usually to be preferred; however, in comparisons with nonlinear molecules,[12] or in comparisons between different electronic states not all having $\Lambda=0$ or $l=0$, K should be used.

In the case of tight spin coupling, one has the electronic quantum number Ω (usually $\Omega=|\Lambda+\Sigma|$), as in diatomic molecules.[1] Ω and l then form a resultant, and **it is recommended (REC. 18)** that this be called P:

$$|\pm\Omega\pm l|=P;$$

if $l=0$, $\Omega\equiv P$, but the notation Ω is usually to be preferred.

III. ROTATIONAL AND OVER-ALL STATES

1. Pure Rotational States

Although the rotational motion of a molecule is never completely independent of its electronic and vibrational motions, nevertheless if the electronic and vibrational state wave functions are *both* totally symmetrical, or at least *nondegenerate*, the molecule may usually be treated as a quasi-rigid rotor in the description of its major rotational properties. This viewpoint will be followed in the present subsection.

(*a*) *Eulerian Angles*

It has been suggested by several people that it would be desirable, in the theoretical discussion of rigid rotor functions, to agree on a single standard way of choosing Eulerian angles. However, since any such standardization should have the agreement of other groups in

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[10] See R. S. Mulliken, Revs. Modern Phys. **14**, 204 (1942); but also see A. D. Walsh, J. Chem. Soc. **1953**, 2266.

[11] H. Bethe, Ann. Physik [5], **3**, 133 (1929).

[12] R. S. Mulliken, Phys. Rev. **60**, 506 (1941).

[13] H. Sponer and E. Teller, Revs. Modern Phys. **13**, 75 (1941).

addition to the spectroscopists, it is proposed that such a cooperative agreement be sought at a later date.

(*b*) *Rotational Constants*

For the three moments of inertia of any molecule and the corresponding spectroscopic constants, **it is recommended** (**REC. 19**) that the symbols I_A, I_B, I_C (or I^a, I^b, I^c if preferred) and A, B, C be respectively used, in such a way that $I_C \geq I_B \geq I_A$ and $A \geq B \geq C$ *in all cases* ($A=h/8\pi^2 cI_A$, and so on, in cm^{-1}; or in Mc/sec); with added subscripts e (for equilibrium), 0 (for $v_1=v_2=\cdots=0$), or $v_1v_2\cdots$ to indicate vibrational quantum numbers, when needed. In general theoretical discussions of symmetric rotor energies, it is convenient to have a single symbol for the *unique* moment of inertia, whether this be I_C (oblate case) or I_A (prolate case). At present I_A is commonly used in both cases; REC. 19 is intended to do away with this confusing practice, which is especially bad when one has to make comparisons with quasi-symmetric asymmetric rotor molecules. However, REC. 19 creates a new, though it is believed minor problem in that, for general discussions of symmetric rotors, symbols are needed for the moments of inertia parallel and perpendicular to the symmetry axis, and for the corresponding rotational constants. No formal recommendation or suggestion is made here to solve this problem, but it is informally suggested that symbols such as $I^{\parallel}$ and $I^{\perp}$, $B^{\parallel}$ and $B^{\perp}$ might be used.

(*c*) *Pure Rotational State Symbols*

It is recommended (**REC. 20**) that the symbol J always be used for the quantum number of total angular momentum exclusive of nuclear spin.

It is recommended (**REC. 21**) that for symmetric rotors, the symbol K be used for the quantum number of axial angular momentum, and that rotational levels be designated by (J,K), e.g. (3,2); and that the same symbol K be used also for asymmetric rotor level-pairs which approximate to levels of symmetric rotors.

For asymmetric rotor levels, **it is recommended** (**REC. 22**) that either of the two following notations be used according to convenience: (1) $J_{K_aK_c}$, e.g. $5_{1,4}$ or $12_{11,2}$, where K_a (prolate K value) is the K value of the given level if the molecule were distorted to a prolate symmetric rotor ($I^c=I^b>I^a$) and K_c is the oblate K value, corresponding to distortion to $I^c>I^b=I^a$; or (2) J_τ, e.g. 12_9, where the "rank" τ runs from $-J$ to $+J$ in order of increasing energy.[14] Notation (1) contains implicitly a classification of the level according to one of the four group-theoretical asymmetric-rotor species, ($++$, $+-$, $-+$, and $--$, or, respectively, A, B_c, B_a, B_b, where, e.g., $+-$ or B_c corresponds to K_c even and K_a odd, and so on); further, $\tau=K_a-K_c$.[14]

2. Fine Structure Levels

(*a*) *General Remarks*

For molecular states in which either the electronic state is degenerate, or degenerate vibrations are excited, or both, there is usually so much interaction between the electronic and/or vibrational and the rotational motion that it is better to emphasize a classification of the combined or "*rovibronic*" (or rovibrational in case the electronic state is totally symmetrical) wave functions and energy levels rather than of purely rotational states. Rovibronic levels often group themselves in such a way that they may be regarded as *fine structures* of rotational levels. The terms rovibronic and rovibrational are not necessarily being recommended here, but, for want of better terms, are being used in this explanatory text to fill an evident need.

Even without rotational motion, fine structures can arise from splittings of degeneracy, usually (1), in harmonics of degenerate vibrations; or (2), in the interaction of degenerate electronic and vibrational states (in linear molecules). Fine structures can also arise (3), in Coriolis interactions between degenerate vibronic states and symmetric-rotor or spherical-rotor angular momentum; or (4), in the interaction of electron spin with rotational motion. In situations (1) and (2), the resulting vibrational or vibronic states are in part nondegenerate and in part degenerate. Each such state which is *nondegenerate* gives rise to a set of rotational levels which may be classified as in Subsection 1; for each such state which is *degenerate*, situation (3) exists. It should be noted that situations (1)–(3) do not arise for asymmetric-rotor molecules, but nevertheless a classification of the rotational levels according to rovibronic as well as rotational species is often useful for these too.

(*b*) *Rovibronic States for Zero Electron Spin*

The quantum numbers J (REC. 20) and K (REC. 17 for linear molecules, REC. 21 for symmetric rotors) are in general really *rovibronic* rather than pure rotational quantum numbers. In general, K corresponds to *total axial* angular momentum. For linear molecules it consists exclusively of vibronic (i.e., electronic and/or vibrational) angular momentum. For symmetric rotors in degenerate vibrational states, it includes in general some vibrational angular momentum, proportional to an index number $\pm l_i$ for each degenerate vibration ν_i (see discussion following REC. 9).

Besides the J and (when appropriate) K and vibrational $\pm l_i$ classification, the species classification of rovibrational states according to their behavior under the rotational subgroup of the vibrational symmetry group of the molecule is important. This is true especially because for nonlinear molecules this same classification determines the behavior of the rovibrational wave function with respect to exchanges of identical nuclei, and so (when nuclear spin functions are also

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[14] King, Hainer, and Cross, J. Chem. Phys. **11**, 27 (1943), have used K_{-1}, K_{+1} with the same respective meanings as K_a, K_c [R. S. Mulliken, Phys. Rev. **59**, 873 (1941)].

considered) governs the statistical weights of rovibrational levels for molecules containing sets of identical nuclei.[15] **It is recommended** (**REC. 23**) that for nonlinear molecules the usual Placzek symbols be used for this rovibrational species classification[15]; and that for symmetrical linear molecules the symbols s and a (symmetric and antisymmetric, respectively, for exchanges of identical sets of nuclei) be used, the same as for diatomic molecules.[1] Following are some examples[15]; it should be recalled that the label E always refers to a twofold degenerate state.

(1) For a molecule of symmetry C_{3v} (rotational subgroup C_3), e.g., the prolate rotor CH_3I, the possible rovibrational species are A and E. For a (7,2) rotational level (see REC. 21) of an E vibrational state, there is a fine structure consisting of one E and two A rovibrational sublevels. And if, for example, the E vibrational state is due to excitation of a single degenerate vibration ν_i with angular momentum index l_i, the E rovibrational sublevel corresponds to $+l_i$ and the two A sublevels to $-l_i$ (see discussion following REC. 9, and see reference 2, Figs. 117–118).

(2) For symmetry D_{3h} (rotational subgroup D_3), e.g., the planar oblate rotor BCl_3, the possible rovibrational species are A_1, A_2, and E. For a (7,2) rovibrational level of an E'' vibrational state, there are one A_1, one A_2, and one E rovibrational sublevels.

(3) For the nonplanar oblate rotor NH_3 (symmetry C_{3v}), the vibrational states are doubled by inversion and the resulting sub-states can be classified according to symmetry D_{3h}; the rovibrational states are then classified under D_3. For a (7,2) rotational level of an E vibrational state, there are one A_1, one A_2, and one E rovibrational sublevels for each of the two sub-states of the inversion doubling.

(4) For an asymmetric rotor of symmetry D_{2h}, e.g. the planar molecule C_2H_4, the rovibrational species are A, B_1, B_2, B_3. For the 3_{+1} rotational level (using the J_τ notation, see REC. 22) of a B_{1u} or B_{1g} vibrational state, the rovibrational species is B_2; for the 3_{+1} level of an A_g or A_u vibrational state, the rovibrational species is B_3.

(5) For a spherical rotor molecule of symmetry T_d, e.g., CH_4, the rovibrational species are A, E, and F. For the $J=6$ rotational level of an E vibrational state, there are two A, three E, and six F sub-levels. In the case of threefold degenerate (F) vibrational states of spherical rotor molecules, Coriolis interaction with rotation causes a primary splitting of the otherwise $3(2J+1)$-fold degenerate rovibrational levels into three components called $F^+(J)$, $F^{(0)}(J)$, and $F^-(J)$; on each of these is superposed a much finer splitting into A, E, and F rovibrational sub-levels.

In addition to the foregoing classification by J and K and by rovibrational species, each rovibrational level of a *linear* or *planar* molecule can be further usefully characterized by its *parity species* (based on its behavior under inversion). **It is recommended** (**REC. 24**) that rovibrational levels be called positive (+) or negative (−), respectively, just as for diatomic molecules, according as their wave functions are symmetric or antisymmetric to inversion.[1] The parity species classification is particularly useful for labeling the two components of l-doublets (or Λ doublets, K-doublets, or Ω doublets: see RECS. 17, 18) of linear molecules.

For nonplanar molecules, each rovibrational level is usually an unresolved doublet (parity degeneracy), so that the parity species classification is useless. In exceptional cases (notably NH_3), these doublets are appreciably split (inversion doubling), one of the two resulting components being +, the other −.

(c) *Rovibronic States for Electron Spin Loosely Coupled*

If a nonzero electron spin is present, but loosely coupled, a second quantum number of total angular momentum is needed in addition to J. **It is recommended** (**REC. 25**) in agreement with recently revised diatomic nomenclature,[1] that this be called N, where, for linear or symmetric-rotor molecules,

$$|\mathbf{K}+\textbf{rotation}|=N,$$

with N replacing J in REC. 21 so that symmetric-rotor levels are indexed by (N,K); and with N similarly taking the place of J in REC. 22 for asymmetric-rotor molecules so that rotational levels are indexed by $N_{K_aK_c}$ or N_τ; further, in all cases,

$$|\mathbf{N}+\mathbf{S}|=J;$$

if $S=0$, N becomes identical with J, but the symbol J is to be preferred. Rovibronic sublevels with different J for a given N constitute spin fine structure. In general, this is superposed on a fine structure associated with N, the same as described in Subsections III 2(a) and III 2(b) except that in these subsections J (expressed or implied) is everywhere to be replaced by N.

(d) *Rovibronic States for Electron Spin Tightly Coupled to Molecular Axis*

A tightly-coupled electron spin is most likely to occur for linear molecules; this case is covered by REC. 18. It can, however, also occur for symmetric-rotor molecules (e.g., in degenerate excited electronic states of CH_3I)[16] in which a rovibronic axial angular momentum contains a large electronic component. It can occur even in quasi-symmetric asymmetric-rotor states, e.g., for nontotally-symmetrical electronic states of ClO_2.[17] In the latter case, the spin is axis-quantized in the magnetic field of K. **It is recommended** (**REC. 26**) that the total resultant axial angular momentum quantum number including electron spin be called P in general, just as in the case of linear molecules (see REC. 18):

$$|K+\Sigma|=P,$$

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[15] See reference 2, Chap. IV.

[16] See R. S. Mulliken and E. Teller, Phys. Rev. **61**, 283 (1942).

[17] See J. B. Coon, J. Chem. Phys. **14**, 665 (1946).

Σ being the quantum number giving the component of the spin S along K, and being essentially the same as the diatomic quantum number Σ. In all cases with tightly-coupled electron spin,

$$|\mathbf{P}+\mathbf{rotation}|=J,$$

in agreement with REC. 20.

3. Stark and Zeeman Effect Levels

In the case of "weak-field" spectra (electron spin zero or tightly coupled, or external field very weak), **it is recommended** (**REC. 27**) that M_N and M_S be used for the rotational and electron spin magnetic quantum numbers. (It is assumed here that the applied field is axially symmetrical.) These quantum numbers are needed especially for radio-frequency spectra, also for the Zeeman and Stark effects in electronic spectra.

4. Nuclear Hyperfine Structure Levels

It is recommended (**REC. 28**) that I be used for the quantum number of the spin of any one nucleus (I_1, I_2, $\cdots$ if there are several nuclear species); T (or T_1, T_2, $\cdots$) for the resultant spin (or spins) of one (or several) sets of identical nuclei in case such resultants are significant; F for the over-all resultant of J and the I's (or T's); M_F for weak-field electric or magnetic quantum number; M_J and a set of M_I's (or perhaps an M_T or M_T's) for strong-field magnetic or electric quantum numbers. In microwave spectra in which only nuclear-quadrupole hyperfine structure is resolved, nuclei having $I<1$ may be ignored and treated as if not contributing to F. In nuclear magnetic resonance all nuclei having $I>0$ must in general be considered as contributing to F.

IV. SPECTRAL TERMS, LINES, AND BANDS

1. Term Formulas and Coefficients

Spectroscopic "terms" (conventionally, in energy/hc, i.e., in cm^{-1} units; or in microwave spectra in Mc/sec frequency units) for polyatomic molecules are conveniently expressed, just as for diatomic molecules,[1] by term formulas in which the total term is written as a sum of parts. **It is recommended** (**REC. 29**) that term formulas be expressed in the general form

$$T=T_e+G(v_1,v_2,\cdots)+F(J,\text{ etc.})\\+\cdots+(\text{fine structure}),$$

using the symbols T for the total, T_e for the "electronic," G for the "vibrational," and F for the "rotational" term, with G and F defined, somewhat arbitrarily, according to RECS. 30 and 31 below.

It is recommended (**REC. 30**) that coefficients ω_i and x_{ij} be defined as indicated in expressions of the following type for vibrational terms;

$$G(v_1,v_2,\cdots)=\sum_i \omega_i(v_i+\tfrac{1}{2}d_i)\\+\sum_i \sum_{k\geq i} x_{ik}(v_i+\tfrac{1}{2}d_i)(v_k+\tfrac{1}{2}d_k)$$

$+\cdots+$(fine structure arising from splitting of any vibrational degeneracy) [d_i=degree of degeneracy in ith vibration mode].

It is recommended (**REC. 31**) that F and the coefficients $A_{[v]}$, $B_{[v]}$, $C_{[v]}$, $D_{[v]}{}^J$ or $D_{[v]}{}^N$, $D_{[v]}{}^{JK}$ or $D_{[v]}{}^{NK}$, $D_{[v]}{}^K$, ζ_i, and α_i be defined as indicated in the following expressions (subscript $[v]$ indicates the ensemble v_1, v_2, $\cdots$).

(1) Linear Molecules with Electron Spin S Zero or Tightly Coupled (see REC. 9)

$$F(J)=B_{[v]}[J(J+1)-K^2]\\-D_{[v]}J^2(J+1)^2+\cdots+(fs,hfs).$$

[Instead of K read Ω or P (see REC. 18) if $S>0$, and for $S=0$ read Λ if $l=0$, or l if $\Lambda=0$ (see REC. 17). In the above, fs refers to fine structure exclusive of any arising from nuclear degeneracy, hfs to hyperfine structure; these are given only to indicate that the rotational term F is defined to include fs and hfs.]

(2) Linear Molecules with Electron Spin Loosely Coupled (see REC. 25)

$$F_i(J)=B_{[v]}[N(N+1)-K^2]-D_{[v]}N^2(N+1)^2\\+\cdots+f_i(N,K)+(fs,hfs).$$

[For K, read Λ if $l=0$, or l if $\Lambda=0$. Use F_1 for $J=N+S$, F_2 for $J=N+S-1$, $\cdots$, just as for diatomic molecules.[1]]

(3) Symmetric-Rotor Molecules (See Subsections III 2(b), (d), also RECS. 9 and 19)

$$F(J,K)=B_{[v]}{}^{\perp}[J(J+1)-K^2]\\+B_{[v]}{}^{\parallel}[K^2-2K\Sigma_i(\pm\xi_i l_i)]-D_v{}^J J^2(J+1)^2\\-D_{[v]}{}^{JK}J(J+1)K^2-D_{[v]}{}^K K^4+\cdots+(fs,hfs).$$

[Instead of K read P (see REC. 26) if $S>0$ and tightly coupled. For $S>0$ and loosely coupled, replace J by N, and add a term $f_i(N,K)$, as in the linear molecule case (2).]

(4) Asymmetric Rotor Molecules

$F(J_\tau)$ or $F(J_{K_a,K_c})$ = complicated expressions[18]; or, if loosely coupled electron spin is present,

$$F_i(J,N_\tau)\text{ or }F_i(J,N_{K_aK_c})\\=\text{complicated expressions}+f_i(N_\tau).$$

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[18] See Reference 2, pp. 210, 370–371, 400, 447, 460, etc.

(5) *B Expressions*

$B_{[v]}=B_e-\Sigma_i\alpha_i^B(v_i+\frac{1}{2}d_i)+\cdots$, with similar expressions for $A_{[v]}$ and $C_{[v]}$; in linear molecules, α_i^B is written simply α_i.

It is recommended (**REC. 32**) that fine structure components be indicated when convenient by subscripts or superscripts attached to F; in particular, by $F_i(J)$ for electron spin fine structure [see (2) above]; or as in $F_a(J)$, $F_b(J)$, $F_{ia}(J)$, etc., using $_a$ and $_b$ respectively (as for diatomic molecules)[1] to denote the lower and upper components in l-doublets and the like (see REC. 24); in the case of threefold degenerate vibrational states of spherical rotor molecules (see Sec. III 2(b), the symbols $F^{(+)}(J)$, $F^{(0)}(J)$, and $F^{(-)}(J)$ are recommended for the three (groups of) rovibrational substates resulting from Coriolis splitting.

It is recommended (**REC. 33**) that symbols for *differences* of vibrational and of rotational term values be used with definitions as illustrated in the following examples[19]:

$$\Delta_1G(v_i)=G(v_1v_2\cdots v_i+1\cdots v_n)-G(v_1v_2\cdots v_i\cdots v_n),$$

$$\Delta_mG(v_i)=G(v_1v_2\cdots v_i+m\cdots v_n)-G(v_1v_2\cdots v_i\cdots v_n),$$

$$\Delta_1F(J)=F(J+1)-F(J),$$

$$\Delta_2F(J,K)=F(J+1,K)-F(J-1,K),$$

$$\Delta_2{}^KF(J,K)=F(J,K+1)-F(J,K-1),$$

$$\Delta_2F_{ia}(J)=F_{ia}(J+1)-F_{ia}(J-1).$$

2. Spectral Lines and Bands

(*a*) *General*

In some branches of spectroscopy, absorption spectra are studied; in others, both emission and absorption spectra. To avoid misunderstandings between workers in absorption and emission spectroscopy, it is advisable to avoid words and symbols related to the ideas of "initial" and "final" levels, but to emphasize the "upper" and "lower" states or levels involved in any spectroscopic transition. For this purpose, **it is recommended** (**REC. 34**) that symbols belonging to the upper level of a transition be labeled with a prime, e.g., J', v_3' (for quantum numbers), T', G', F' (for spectroscopic terms); and those belonging to the lower level with a double prime, e.g., J'', v_3'', T'', G'', or F''. For the *difference* in any quantum number between an upper and a lower level, **it is recommended** (**REC. 35**) that symbols such as ΔJ, meaning $J'-J''$, or Δv_3, meaning $v_3'-v_3''$, or ΔK, or ΔN, be used. RECS. 34 and 35 are in agreement with those for diatomic spectra.[1]

To designate any spectroscopic transition, **it is recommended** (**REC. 36**) that suitable upper state term symbols or quantum numbers be written first, corresponding lower state symbols second, separated by a minus sign or dash[1] to indicate subtraction; for example,

$$T'-T'';$$

$$G(v_1'v_2'\cdots)-G(v_1''v_2''\cdots);$$

$$F(J',K')-F(J'',K'');$$

$$(J_{K_aK_b})'-(J_{K_aK_b})'';$$

or instead of a minus sign an arrow to left or right may be used if one wishes to designate the emission or absorption character of the transition, as for example

$$J_{\tau'}'\leftarrow J_{\tau''}''\quad\text{or}\quad 10_5\leftarrow 9_4,$$

$$F_1(J+1,K)\leftarrow F_1(J,K),$$

for certain absorption transitions, and

$$J_{\tau'}'\rightarrow J_{\tau''}''\quad\text{or}\quad 10_5\rightarrow 9_4,$$

$$F_1(J+1,K)\rightarrow F_1(J,K),$$

for corresponding emission transitions.

The wave number (cm^{-1}) or frequency (in Mc/sec) of any transition is usually given by

$$\nu=T'-T'',$$

with appropriate specialization of T' and T'' to correspond to the particular case. But in the special case of Raman spectra, the wave number which is directly observed is given by

$$\nu=\nu_{\text{exc.}}\mp(T'-T''),$$

for "Stokes" and "anti-Stokes" lines or bands, respectively.

(*b*) *Bands and Electronic Transitions*

For bands in vibrational spectra, **it is recommended** (**REC. 37**) that designations such as

$$\nu_1+2\nu_2-\nu_3$$

for a certain combination band, or

$$2\nu_2-\nu_2$$

for a "hot" fundamental, be used when convenient. Similar designations might also be used for bands in electronic spectra, but the attribution to upper or lower electronic states must then be indicated, as for example by

$$\nu_1'+2\nu_2'-\nu_3''.$$

It is recommended (**REC. 38**) that the wave number or frequency of any spectroscopic transition be expressed (corresponding to RECS. 29–31 for term symbols and formulas) in the general form

$$\nu=\nu_e+\nu_v+\nu_r,$$

where

$$\nu_e=T_e'-T_e'';\quad \nu_v=G'-G'';\quad \nu_r=F'-F'',$$

and that for the *origin* of any vibrational or electronic

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[19] In reference 1, the definitions $\Delta_1F(J+\frac{1}{2})=F(J+1)-F(J)$ and $\Delta_1G(v+\frac{1}{2})=G(v+1)-G(v)$ are recommended for diatomic molecules, but the often used simpler form recommended here seems preferable. The present definition of $\Delta_1F(J)$ is used in reference 2.

band, the symbol ν_0 be used:

$$\nu_0=\nu_e+\nu_v;$$

ν_e denotes the *origin of a band system*. REC. 38 corresponds to the same notation as for diatomic spectra.[1]

In diatomic spectra, one distinguishes between individual "bands," each corresponding to a definite pair of quantum numbers v', v'', and "band systems," each composed of an ensemble of bands associated with a particular electronic transition. In polyatomic spectra, often (a), the individual bands of an electronic transition are so numerous and strongly overlapping that it is difficult or impossible to distinguish them individually, or (b), the electronic transition gives rise only to continuous absorption; in both these situations, the entire spectrum of the electronic transition is commonly called a band. **It is recommended** (**REC. 39**) that the word "band" be reserved for definite individual bands, and that "electronic transition" or "transition" be used for the entire spectrum, whether discrete, pseudo-continuous, or strictly continuous, associated with an electronic transition; or "band system" if the spectrum consists of discrete bands.

(*c*) *Band structures*

In vibrational (infrared and Raman) and electronic bands, long series of lines (*branches*) occur for which it is convenient to have standard designations. **It is recommended** (**REC. 40**) that the letters O, P, Q, R, S be used to designate band branches with $\Delta J=-2, -1, 0, +1, +2$ respectively (see REC. 35); with corresponding left superscript O, P, Q, R, or S (e.g., ${}^QP$ to denote $\Delta K=0$, $\Delta J=-1$) to denote ΔK in the case of symmetric-rotor and quasi-symmetric asymmetric-rotor molecules; and in general that band branches, subbranches, and fine structures be designated as in Herzberg's book.[20]

In case a *loosely-coupled* electron spin S is present, **it is recommended** (**REC. 41**) that numerical subscripts be added to indicate spin fine structure, for example ${}^PR_{12}(J)$ for $\Delta K=-1$, $\Delta J=1$, and an F_1 upper and an F_2 lower state [hence $\Delta N=0$ if $S=\frac{1}{2}$; see REC. 31(b)]; but for linear molecules, the left superscript is to be omitted, since K is then a vibrational or electronic rather than a proper rotational quantum number (see REC. 17).[21]

Branch symbols are needed in vibrational and in rotational Raman spectra as well as in vibrational and electronic bands. For vibrational Raman bands,

$$\nu=\nu_{\text{exc.}}\mp[(G'-G'')+(F'-F'')],$$

with the $-$ or $+$ sign for Stokes and anti-Stokes bands respectively. REC. 40 is applicable here, for both Stokes and anti-Stokes bands; the definitions $\Delta J=J'-J''$, $\Delta K=K'-K''$ should be kept in mind. A corresponding recommendation has been made[1] for diatomic Raman spectra.

For pure *rotational* Raman bands,

$$\nu=\nu_{\text{exc.}}\mp(F'-F'').$$

At least in the case that F depends only on J, ΔJ is necessarily positive (since $F'>F''$ by definition); therefore **it is recommended** (**REC. 42**) that the symbols R, S be used for $\Delta J=+1$ and $+2$ for *both* Stokes and anti-Stokes branches, even though the Stokes branches with $\Delta J=+1$ and $+2$ simulate P and O branches.[22] A corresponding recommendation has been made[1] for diatomic Raman spectra.

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[20] See reference 2, Chap. IV.

[21] For diatomic band branches (see reference 1) a left superscript O, P, Q, R, or S is used to designate ΔN when a loosely coupled electron spin is present. However, this practice, though convenient, is not really necessary, since when ΔJ and the spin subscripts are given, the value of ΔN is determined. To avoid confusion between ΔK and ΔN, it seems best in polyatomic spectra to use the left superscript only to denote ΔK of nonlinear molecules.

[22] See reference 5, page 35 and footnote 17 there.