

LETTER TO THE EDITOR

The Labeling of Parity Doublet Levels in Linear Molecules

J. M. BROWN,¹ J. T. HOUGEN,² K.-P. HUBER,³ J. W. C. JOHNS,³ I. KOPP,⁴
H. LEFEBVRE-BRION,⁵ A. J. MERER,⁶ D. A. RAMSAY,³ J. ROSTAS,⁵
AND R. N. ZARE⁷

The rotational energy levels of diatomic and linear polyatomic molecules often occur in closely spaced pairs of opposite parity. In this situation the lower levels of each pair usually form a characteristic set (for example, it may be possible to describe them all with a single energy level expression) even though their parities alternate with the rotational quantum number; similarly, the upper levels of each pair form a second distinct set. Mulliken (1) introduced a labeling scheme in order to distinguish between these sets for diatomic molecules; his labels are *c* and *d* for case (a) and case (b) states, and *e* and *f* for case (c) states. However, his rules for assigning these labels require care in their application and are hard to memorize. Herzberg (2) introduced an alternative definition of *c* and *d* for singlet states of diatomic molecules which differs from that of Mulliken for odd values of Λ . Some authors have extended this system to multiplet states, though the rules for such an extension have never been clearly defined. Other authors have used the labels *c* and *d* to denote the upper and lower series of parity doublets respectively, or the converse. The confusion which has arisen in the literature is unfortunately widespread and a reexamination of the problem is clearly needed. It is understandable that molecular spectroscopists have been reluctant to advocate yet another labeling scheme, but fortunately there now appears to be a strong consensus in favor of one particular scheme and it is the purpose of this letter to draw attention to it.

In a discussion of the rotational levels in $\Omega = \frac{1}{2}$ states, Kopp and Hougen (3) introduced a simple labeling scheme for molecules with an odd number of electrons (half-

¹ Department of Chemistry, The University, Southampton SO9 5NH, U. K.

² National Bureau of Standards, Washington, D. C. 20234, U. S. A.

³ Division of Physics, National Research Council of Canada, Ottawa, Canada K1A 0R6.

⁴ Institute of Physics, The University, S-11346 Stockholm, Sweden.

⁵ Laboratoire de Photophysique Moléculaire du CNRS, Bâtiment 213, Université de Paris-Sud, 91405-Orsay, France.

⁶ Department of Chemistry, University of British Columbia, Vancouver, Canada, V6T 1W5.

⁷ Department of Chemistry, Columbia University, New York, N.Y. 10027, U. S. A.

integral J values) using the symbols e and f . Their convention is:

levels with parity $+(-1)^{J-\frac{1}{2}}$ are e levels, and
 levels with parity $-(-1)^{J-\frac{1}{2}}$ are f levels,

where J is the quantum number for *total* angular momentum, omitting nuclear spin⁸. A complete scheme of labeling for all multiplicities requires a similar convention to be established for molecules with an even number of electrons (integral J values). We therefore recommend that, for such molecules,

levels with parity $+(-1)^J$ be called e levels, and
 levels with parity $-(-1)^J$ be called f levels.

In other words, e and f levels transform in the same way as the rotational levels of ${}^1\Sigma^+$ and ${}^1\Sigma^-$ vibronic states, respectively.

The principal advantage of the e and f labels is that they are independent of the coupling case, since they depend only on the total angular momentum J and the parity of a particular state, both of which are well defined in field-free space. The scheme leads to the following simple rules:

- (a) *Selection rules for transitions induced by electromagnetic radiation.* Electric dipole transitions obey the selection rules $\Delta J = 0, \pm 1$, and $+ \leftrightarrow -$. In terms of e and f labels, these rules become

$$\begin{aligned}\Delta J &= 0, e \leftrightarrow f, \\ \Delta J &= \pm 1, e \leftrightarrow e, \text{ and } f \leftrightarrow f.\end{aligned}$$

Corresponding rules can easily be established for transitions induced by the magnetic dipole moment, electric quadrupole moment, etc.

- (b) *Selection rules for perturbations.* Perturbations are governed by the selection rules $\Delta J = 0, + \leftrightarrow +$, and $- \leftrightarrow -$, which when reexpressed become simply

$$\Delta J = 0, e \leftrightarrow e, \text{ and } f \leftrightarrow f.$$

Since the labeling scheme is based solely on parity and J value, these rules are valid for all situations, that is for perturbations between states of the same or different multiplicity or in the limit of strong spin-orbit coupling (case (c)).

In addition, because of its simple dependence on J value and parity, the present convention is easier to remember than Mulliken's. The relationships between the present e and f labels and Mulliken's labels are given in Table I.

As an example of the simplicity of the e, f scheme, consider the correlation of the levels of a regular case (a) state through case (b) to an inverted case (a) state. By definition, the e, f labeling remains unchanged. Mulliken's scheme, which is based on a case (b) representation where N is a good quantum number, achieves the same end, but to obtain consistency in the case (a) limit he had to interchange the parity labels at the lowest J values in certain cases, e.g. for $J = \frac{1}{2}$ levels of a regular ${}^2\Pi$ state (see (1, n. 58)). The usefulness of e and f as opposed to c and d is most apparent in calculations of energy levels and perturbations. In all cases the Hamiltonian matrix factorizes into

⁸ Inclusion of nuclear spin introduces no further complications provided the hyperfine interactions are small compared with the separations of electron spin component levels.

TABLE I
THE RELATIONSHIP BETWEEN THE PRESENT SCHEME AND THE MULLIKEN LABELS

Present scheme	Mulliken (<i>I</i>)			
	Case (a) and (b)		Case (c)	
	$S = 0, \frac{1}{2}, 2, 2\frac{1}{2}, \dots$ $\Lambda = 0^\pm, 2, 4, \dots$ or $S = 1, 1\frac{1}{2}, 3, 3\frac{1}{2}, \dots$ $\Lambda = 1, 3, 5, \dots$	$S = 0, \frac{1}{2}, 2, 2\frac{1}{2}, \dots$ $\Lambda = 1, 3, 5, \dots$ or $S = 1, 1\frac{1}{2}, 3, 3\frac{1}{2}, \dots$ $\Lambda = 0^\pm, 2, 4, \dots$	$\Omega = 0^\pm, \frac{1}{2}, 2, 2\frac{1}{2}, \dots$	$\Omega = 1, 1\frac{1}{2}, 3, 3\frac{1}{2}, \dots$
$F_{i=\text{odd}}$ $F_{i=\text{even}}$ <i>c</i> <i>d</i>	$F_{i=\text{odd}}$ $F_{i=\text{even}}$ <i>d</i> <i>c</i>	<i>e</i>	<i>f</i>	
<i>e</i>	<i>d</i>	<i>c</i>	<i>e</i>	
<i>f</i>	<i>c</i>	<i>d</i>	<i>f</i>	

Note: ${}^1\Sigma^+$ and 0^+ states have only *e* levels; ${}^1\Sigma^-$ and 0^- states have only *f* levels. For Σ states of higher multiplicity both *e* and *f* levels occur, although each F_i sublevel contains either *e* or *f* levels but not both. The labels *i* in F_i take the values $1, 2, \dots, 2S + 1$ for $J = N + S, N + S - 1, \dots, N - S$. Note that in regular multiplet states the values of N corresponding to the lowest J values are not always immediately obvious; the *e, f* labeling of the levels, however, is unambiguous.

two submatrices which may be identified directly with the *e* and *f* levels, but not necessarily with the upper and lower components of the doublet, or with Mulliken's *c* and *d* labels. For example, in a ${}^3\Pi$ state the *e* submatrix contains Mulliken's *c* levels for $\Omega = 0$ and 2 and his *d* level for $\Omega = 1$. Perturbing states are readily accommodated by adding extra rows and columns to the *e* and *f* submatrices, as required.

The whole discussion so far assumes that the parity and J value of a rotational state have been assigned. The J value can be determined experimentally, but the parity can only be established if it is possible to refer the level, either directly or indirectly, to a Σ^+ or Σ^- state, an assignment which is usually made on theoretical grounds. For example, in linear polyatomic molecules the assignment of Σ^+ and Σ^- vibrational states is straightforward, so that the labeling of the parity doublets in the bending fundamentals follows immediately; thus, since the bending frequency in a triatomic molecule is almost invariably the lowest, the *f* levels usually lie above the *e* levels. The majority of infrared spectroscopists use *c* and *d* labels and most of them appear to follow Herzberg's definition; for *singlet* states, which are those normally encountered in infrared spectroscopy, Herzberg's *c* and *d* labels correspond to our *e* and *f* respectively.

There may well be occasions, particularly early in a spectral analysis, when it is not possible to assign *e* and *f* labels with any confidence. In this situation, it is probably best to follow the recommendations of Jenkins (4) and Mulliken (5) and describe the lower energy level in any related pair as an *a* level and the higher as a *b* level, reserving the *e* and *f* labels for cases where the parities have definitely been established.

In conclusion, the *e* and *f* labeling scheme presented here has two great virtues, namely simplicity and generality. Furthermore, this scheme has been fully endorsed by Drs. G.

Herzberg and R. S. Mulliken. We believe that the case in favor of its adoption is overwhelming.

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