# Chirality and the weak current interactions in molecular spectroscopy: a symmetry analysis

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## Abstract

The influence of the parity violating weak current interactions between nucleons and electrons is discussed with reference to molecular spectroscopy and the enantiomeric energy inequivalence. Several novel effects are suggested, based on simple symmetry arguments applied to isolated molecules and ensembles. By measuring these effects spectroscopically, in the laboratory and in the spectra of distant galactic matter receding near the velocity of light, avenues may be found which lead to a new appreciation of the role of the W boson mediator in molecular spectroscopy and dynamics.

## INTRODUCTION

This paper addresses the chirality of combined molecular rotation and translation, with a view to suggesting new spectral methods of detecting the effect of the weak current interactions [1–5] on the absorption and scattering of electromagnetic radiation from molecular matter. The symmetry arguments used are based on the recent definition of true chirality by Barron [6], and in particular the statement that the space inverted enantiomers of truly chiral systems show a parity-violating energy difference [7] due to weak current interactions in the relevant hamiltonian. True chirality has been defined by Barron as being exhibited by systems that exist in two distinct enantiomeric states that can be interconverted by the space inversion operation $(X, Y, Z) \rightarrow (-X, -Y, -Z)$ but cannot be interconverted by time reversal combined with proper spatial rotation [6]. Thus, two vectors generate true chirality if the product of their symmetry representations is negative to parity reversal and positive to time reversal. If we seek to use the Barron definition with molecular ensembles, group theoretical statistical mechanics [8–10] implies the need for point group theory in the laboratory frame $(X, Y, Z)$ of the isotropic ensemble at reversible

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thermodynamic equilibrium. (Special consideration is given to the kinetics of systems out of equilibrium [11].) In the language of g.t.s.m., Barron's definition translates as follows.

In the point group $R_h(3)$ of an isotropic ensemble of molecules at reversible thermodynamic equilibrium, true chirality is generated by the product of irreducible representations

$$\Gamma(A)\Gamma(B)=D_u^{(1)}D_g^{(1)}=D_u^{(0)}+D_u^{(1)}+D_u^{(2)} \tag{1}$$

of a polar vector $A$ and an axial vector $B$ provided that the product is also positive to time reversal.

The symmetry representation in eqn. (1) may for example be that of the time cross-correlation function (c.c.f.) between molecular centre-of-mass translational ($v$) and angular ($\omega$) velocity, denoted in general by the three by three tensor

$$C_{v\omega}=\langle v(0)\omega(t)\rangle \tag{2}$$

This c.c.f. is chiral, but not visible, because g.t.s.m. requires [8–10] that the ensemble average, to exist at equilibrium, must include the totally symmetric irreducible representation (t.s.r.) $D_g^{(0)}$ of $R_h(3)$.

If the molecules of the ensemble are themselves chiral, the point group of the ensemble becomes $R(3)$, whose t.s.r. is $D^{(0)}$. The symmetry representation of the c.c.f. $C_{v\omega}$ in $R(3)$ is $D^{(0)}+D^{(1)}+D^{(2)}$, which includes its t.s.r. once. This implies that the a.c.f. $\langle v(0)\cdot\omega(t)\rangle$ may exist in frame $(X, Y, Z)$ in an ensemble of chiral molecules. Furthermore, chiral external fields [12–15] may induce the existence in frame $(X, Y, Z)$ of all nine elements of the c.c.f. in ensembles both of achiral and chiral molecules (third principle [8–10] of g.t.s.m.).

The $D$ symmetries of the point group $R(3)$ may also be used to define chirality in a simultaneously rotating and translating object on the macroscopic or molecular scale.

THE CHIRALITY OF AN INDIVIDUAL MOLECULE THAT IS SIMULTANEOUSLY ROTATING AND TRANSLATING

An individual achiral molecule that is simultaneously rotating and translating generates dynamical chirality because the product of symmetry representations within the appropriate point group in $(X, Y, Z)$ of the molecular linear and angular velocities is odd to parity inversion and even to time reversal. However, if the molecule is dynamically chiral, the parity inversion $(X, Y, Z)\rightarrow(-X, -Y, -Z)$ takes it to its enantiomer, an energetically different entity. The appropriate point group with which to describe the chirality generated dynamically is therefore $R(3)$, which applies to the individual molecule. (The point group of the ensemble of achiral molecules is still $R_h(3)$.) The symmetry representation of the individual molecular dynamical chirality within its $R(3)$

point group is $D^{(0)} + D^{(1)} + D^{(2)}$, which includes the t.s.r. $D^{(0)}$ once. This implies that molecular dynamical chirality due to combined rotation and translation supports the existence in frame $(X, Y, Z)$ of pseudoscalar quantities such as the rotation of the plane of polarised radiation interacting with the individual molecule.

Therefore, if a simultaneously rotating and translating achiral molecule could be isolated in frame $(X, Y, Z)$, the eigenstates $|JKM\rangle$ and $|JK-M\rangle$ will no longer have the same energy because $M$ is the rotational quantum number of molecular angular momentum about the $Z$ axis of frame $(X, Y, Z)$. Reversing the angular momentum and keeping the direction of translation constant generates the opposite dynamical enantiomer, whose energy is different because of the parity violating [6] weak current interaction between the electrons and nucleons of the molecule.

In an ensemble of such molecules, however, no rotation will be observed, because in the appropriate point group $R_h(3)$ the t.s.r. must be a true scalar, and non-vanishing ensemble averages must be $D_g^{(0)}$. There is no optical rotation therefore in a thermodynamically equilibrated ensemble of achiral molecules. If we were able to isolate one achiral molecule and observe it in complete isolation we would see optical rotation due to combined rotation and translation. If we could stop the molecular translation, the optical rotation would again disappear, because pure rotation is not dynamically chiral [6]. Pure rotational states of an achiral molecule are achiral, provided that the centre-of-mass translational velocity relative to the observer is zero.

THE EFFECT OF IMPOSED EXTERNAL TRANSLATION

If the ensemble of rotating and translating achiral molecules were itself translating unidirectionally the ensemble would be subjected to an influence whose symmetry in $R_h(3)$ is $D_u^{(1)}$ and in $R(3)$ is $D^{(1)}$. Thermodynamically averaged quantities which reduce in either point group with these $D$ representations exist in the steady state under the externally imposed symmetry influence according to the third principle of g.t.s.m. [8–10]. In the ensemble, the mean velocity $\langle \mathbf{v} \rangle$ is imparted to the ensemble with symmetry $D_u^{(1)}$, and for each individual rotating and translating molecule, the velocity $\mathbf{v}$ is imparted to the centre of mass with symmetry $D^{(1)}$. If it were possible to isolate a single molecule and consider what happens to its chirality we would observe spectral changes produced by the following argument.

The isolated molecule is a dynamically chiral object. Imparted with a unidirectional velocity in $(X, Y, Z)$, it would move away from the observer with a helicity, which would increase in proportion to $v/c$, where $c$ is the velocity of light. The parity violating optical activity will become increasingly stable [6] as the molecule approaches the speed of light. The energy difference between $|JKM\rangle$ and $|JK-M\rangle$ will increase in proportion to $v/c$, as will the optical

rotation observable in each quantum absorption line. We would expect to see a splitting as the degeneracy of $|JKM\rangle$ and $|JK-M\rangle$ is lifted. The optical rotation for $|JKM\rangle$ will be opposite from that for $|JK-M\rangle$, but not equal. Both effects are due to the parity violating weak current interactions [6], a parity violating energy difference between space inverted enantiomers of chiral entities. In this case the chiral entity is the dynamically chiral molecule, whose natural (thermal) rotation and translation is superimposed on an external unidirectional translation close to the speed of light.

The latter can be achieved in practice by observing the microwave and far-infrared spectra of far-distant galaxies, assuming that these are receding from earth at close to the speed of light, and assuming that their stellar and interstellar matter contains dipolar molecules. Comparison of these spectra with those obtained in the laboratory reveals the spectral effects of the parity violating energy difference. The spectrum from the distant galaxy is much more effectively enantiomeric than that in the laboratory, due to translation close to the speed of light producing relativistic helicity [6], which is dynamically chiral.

A practical problem is that it is not easy to isolate a molecule from its ensemble, and in the ensemble, the imposition of linear velocity alone, with $D_{\mathrm{u}}^{(1)}$ symmetry, is not enough to produce true chirality and optical activity. To produce true chirality in an ensemble of molecules we need either: (a) a chiral external field [8] applied to achiral molecules, or (b) chirality in the molecular framework itself.

In order to see parity violating spectral effects in an ensemble of molecules the radiation from the distant galaxy entering our spectrometer would have to be treated with a magnetic field, which is time odd, and which has $D_{\mathrm{g}}^{(1)}$ symmetry in $R_{\mathrm{h}}(3)$ of the ensemble of achiral molecules. The magnetic field, combined with the velocity imposed by the receding galaxy, the source of the radiation, amounts to a chiral influence whose symmetry in $R_{\mathrm{h}}(3)$ of the ensemble of framework-achiral molecules is the r.h.s. of eqn. (1). In the unlikely event that radiation from chiral molecules could be picked up from the distant galaxy, we could dispense with the magnetic field.

The radiation entering a spectrometer from a rotating stellar object of a distant galaxy receding near the speed of light should be chiral. The parity violating energy differences due to this chirality should become discernible when the spectrum is compared with its counterpart in the laboratory. The radiation should be optically active and this effect is different from the well-known red shift, a Doppler effect.

PARITY VIOLATING SPECTRAL EFFECTS IN THE LABORATORY

The technology for the observation of microwave and far-infrared quantum absorptions from distant galactic matter may not be available, and the galactic

radiation may be too weak, or may contain no spectral features of the right type. This removes the advantage of working with molecular matter moving close to the speed of light, in that the effects we are looking for are in proportion to $v/c$.

In the laboratory, parity violating spectral effects are much smaller, but could be detected in principle in situations such as the following.

(1) In the vibration-rotation spectrum of an isolated achiral molecule. The dynamical chirality is generated by time-odd, parity-odd vibration and time-odd, parity-even rotation. In an ensemble, the effect will, however, be averaged out. Thus, vibration-rotation quantum lines of an isolated achiral molecule may be expected to be optically active. Even in this case, collisions with the walls of the measuring cell might remove the chirality by "scrambling" the directions of the linear and angular molecular momenta.

(2) By comparing directly the very high resolution spectra (e.g. infrared/radio frequency double resonance) of enantiomers of chiral molecular ensembles at high spectral resolution. This method has been equivocal so far [16] but is basically sound.

(3) By creating dynamical chirality in an ensemble with external fields of the appropriate symmetry. In both chiral and achiral ensembles dynamical chirality can be generated by imposing helicity with a powerful circularly polarised laser field. The imposed helicity is dependent in the intensity of the laser field, which can be applied in pulse trains to prevent heating. A laser field with right handed helicity imparts dynamical chirality to an ensemble of achiral molecules, and in this case the ensemble becomes optically active. A laser field with precisely the opposite helicity results in the dynamical enantiomer, which is energetically different because of the parity violating weak currents in each molecule of the ensemble. These energy differences could in principle be observed by tuning the circularly polarised laser frequency to an absorption line of the microwave or infrared spectrum of the dilute gas and inducing simultaneous Stark and Zeeman splitting with the electric and magnetic fields of the laser. The splitting should be different for the right and left circularly polarised laser fields due to the imposed enantiomeric energy inequivalence. The chances of seeing this experimentally depend on the use of ultra-high resolutions and precise frequency-locking of the circularly polarised laser to an absorption line which can be split by the combined Stark or Zeeman effects. If the molecules of the dilute gas are themselves chiral we have at least four possibilities: (a) right handed laser to right handed molecular ensemble; (b) left to left; (c) left to right; (d) right to left. The laser induced Stark/Zeeman splittings are different in all four cases because we are dealing with both dynamical and molecular-framework chirality.

(4) Other candidates for the spectral detection of enantiomeric energy in equivalence (dynamical or structural or a combination of both) include the "inverse Faraday effect" where magnetisation is induced [17] by a circularly

polarised laser field. The magnetisation should be minutely different for right and left handed lasers, because these are space inverted enantiomeric states with a parity violating energy difference imparted to the magnetisation.

(5) There are many other effects of this kind due to the presence in electrons and nucleons of molecules of weak current interactions mediated by the W boson. One final example given in this brief survey is the optical Kerr effect induced by enantiomeric electromagnetic radiation (i.e. circularly polarised lasers replacing the usual linearly polarised lasers). The ellipticity acquired by the measuring beam should be minutely different for right- and left-handed inducing lasers.

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