[Review]

Temperature-induced Phase Transitions in Chiral Amino Acids—Search of Spontaneous Parity-Breaking and Restoration *

WANG, Wen-Qing MIN, Wei GONG, Yan

(Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871)

Abstract The effects of temperature on the parity-violating entropy and energy differences of chiral molecules are investigated both theoretically and experimentally. Statistical thermodynamics calculations indicate the possible occurrence of sign reversal of parity-violating entropy difference at different temperatures, which is supported by temperature-dependent polarized Raman spectra of D-alanine and L-alanine. An incoherent spontaneous symmetry breaking is proposed to describe the bifurcation mechanism between mirror-image systems at the critical temperature, in which usually violated parity symmetry will be dynamically restored again. An asymmetric double-well potential with a tiny parity-violating energy difference(PVED) in the depths of the two potential wells showed that the presence of PVED can lead to the enrichment of L-form amino acid. Tunneling dynamics of amino acids with PVED provides a plausible mechanism for much faster development of homochirality.

Keywords: Temperature effect, Temperature-conformation-PVED relation, Parity-violating entropy difference, Tunneling dynamics, Alanine enantiomers

Chirality exists in our universe, which is inherently chiral, at different levels of size. Nowadays, few topics as the research of the chirality of nature have surpassed the pure chemical threshold, interlocking the physical and life sciences and attracting the interest of the scientists over generations^[1-11]. From a conceptual view, molecular chirality is important in relation to fundamental physics and chiral bias in molecular biology, in particular to the underlying violation of symmetry and the structure of our universe. Early in 1876, van't Hoff^[12] pointed out: for the invariance of the mechanical laws that govern molecular motion under the space inversion operation, the heat of formation and the entropy of enantiomers of chiral molecules and thus the Gibbs energy must be exactly equal at all temperatures. This fundamental symmetry of space had not been doubted until the emergence of that classical paper "Question of parity conservation in weak interactions" and the following experimental evidence in ⁶⁰Co β decay^[13-14].

Rein^[15] and Letokhov^[16] first suggested that the electroweak

interaction, a unified description of the electromagnetic and weak interaction, would lift the degeneracy between enantiomers predicted by quantum electrodynamics. For a chiral molecule, we can consider two right-handed and left-handed states. If a molecule can change its configuration by tunnel effect, which was introduced by Hund^[17] in his treatment on molecular chirality, mirror symmetry is dynamically restored and energy eigenstates are the parity eigenstates. If the potential barrier is very high (negligible tunnel effect), enantiomeric left- and right-handed species are stable, and handedness as parity is a good quantum number for energy eigenstates. Due to the parity-violating weak interaction, the Hamiltonian matrix will remain diagonal only in the handedness-eigenstate basis, and the energy difference appears between left and right enantiomers(Fig.1).

The recent *ab initio* calculations^[19] showed that the value of PVED was larger by orders of magnitude than previously anticipated. This remarkable progress has stimulated extensive speculations on the influence of molecular asymmetry on the preferred

Received: March 14, 2005; Revised: April 26, 2005.

Correspondent: WANG, Wen-Qing (E-mail: wangwqchem@pku.edu.cn; Tel: +8610-

62752457). *The Project Supported by NSFC(20452002) and NKBRP (2004-36)

Fig.1 Mirror image of D- and L- enantiomers ^[18]

$$2|E^{PV}| = |\langle \psi^L | H^{PV} | \psi^L \rangle - \langle \psi^D | H^{PV} | \psi^D \rangle| = 2|\langle \psi^L | H^{PV} | \psi^D \rangle|$$

selection of L-amino acids and D-sugars in the biochemistry of the evolution of life, although this topic has been the subject of controversial debate with a variety of alternative suggestions^[4,8,10].

In addition to the subtle and complex effects on the origin of biochirality, experiments on chiral molecules are of particular importance, since the symmetry violation of molecules could lead to observable differences of enantiomers. There have been a number of experimental attempts to measure this parity-odd effect. In 1999, Daussy *et al.*^[20] developed a saturation spectroscopy experiment to test the enantiomers of chiral CHFCIBr giving different spectra because of the parity violation associated with neutral currents in the weak interaction between electrons and nuclei. The frequencies of saturation resonance of separated CHFCIBr have found to give $\Delta\nu$ within 13 Hz ($\Delta\nu/\nu=10^{-13}$), which is five orders of magnitude greater than the effects theoretically anticipated. In 2002, they reduced this difference with a small estimated relative uncertainty of $\Delta\nu_{PV}=(4.2\pm0.6\pm1.6)$ Hz^[21]. Lahamer *et al.*^[22] reported the Mössbauer spectra for L- and D-enantiomers of the $\text{Fe(phen)}_3\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 8\text{H}_2\text{O}$ complex, which showed a small energy shift of (0.004 ± 0.002) nm (1.9×10^{-10} eV). Due to the tiny differences and the experiment being performed on crystal^[23], it seems to be difficult to guarantee that the difference is intrinsically from parity violation and not from some parasitic effects arising from intermolecular interactions or minor impurities in sample^[9].

Another approach was raised by Harris and Stodolsky^[24-25]: If the barrier to stereomutation was such that the tunneling splitting and parity violation energies were about equal, one might experimentally observe a time-dependent oscillation of optical activity with an amplitude significantly different from Hund's prediction for a symmetrical potential. Since the optical activity is difficult to observe at the high dilution in a molecular beam, this remained only a theoretical possibility.

In sharp contrast to Z^5 scaling law of heavy atom, which has been extensively discussed^[26], the effect of temperature as a

control parameter on parity violation in the experiment has so far received little attention. However, Wang *et al.* performed a number of temperature-dependent measurements on single crystals of D- and L-alanine, which exhibit obvious phase transition in specific heat^[27-28], DC-mass susceptibility^[29], solid state NMR spectra^[30] and ultrasonic attenuation around 250 K^[31]. In 2004, Barthes *et al.*^[32] found a micro-transition in L-alanine between 243~246 K which coincided with the observation of the ultrasound attenuation at 247 K by Wang *et al.* Sullivan *et al.*^[33] reported that a small endothermic transition occurs in both D- and L-alanine around 270 K and revealed an endothermic peak of D-valine at 271 K but none for L-valine by differential scanning calorimeters which also appeared in Wang's first experimental test due to the low sensitivity^[34]. Sullivan's finding on Raman spectroscopy(294~271 K), ^{13}C ssNMR spectroscopy (298~248 K) and magnetic susceptibilities (4~300 K) in D- and L-alanine, did not concur with Wang's data. Since the work in this direction has been of intense interest and controversy over the past several years^[11, 23, 35-36], it is time to discuss critically these facts in the light of a broader concept of molecular parity violation in altering the temperature.

The present paper will focus on the special significance of temperature effect on PVED combining theories and experiments. Potential physical consequences of cooperative and simultaneous vanishing of PVED in condensed-phase, and its possible underlying relation with spontaneous symmetry breaking are discussed. Particularly, a kinetic model at bifurcation point (~250 K) between D- and L-alanine is suggested. Before address the effect of temperature on PVED, we had better investigate its effect on parity-violating entropy difference, which might provide a quantitative and revelatory description about the role of temperature-induced phase transitions.

1 The effect of temperature on parity-violating entropy difference ($\Delta_e S^0$)

$$D \leftrightarrow L$$

$$\Delta_e G^0 = \Delta_e H^0 - T\Delta_e S^0$$

$$K = \exp(-\Delta_e G^0/RT) = \exp(-\Delta_e H^0/RT + \Delta_e S^0/R)$$

The Gibbs free energy was obtained by applying standard statistical mechanics techniques. Temperature dependence of thermodynamic state functions was calculated from the molecular partition function (Q_{tot}). The total energy E_{tot} of a molecule is separable in the degrees of freedom for the translational, electron-

ic, vibrational and rotational parts.

$$E_{\text{tot}}=E_{\text{trans}}+E_{\text{el}}+E_{\text{vib}}+E_{\text{rot}}$$

The partition function Q_{tot} is given by the product:

$$Q_{\text{tot}}=Q_{\text{trans}} \cdot Q_{\text{el}} \cdot Q_{\text{vib}} \cdot Q_{\text{rot}}$$

We neglected the electronic contribution to the entropy^[39]. The temperature-dependent equilibrium constant $K(T)$ for the stereomutation is given by:

$$K(T)=\frac{Q_{\text{trans}}^{\text{D}} \cdot Q_{\text{vib}}^{\text{D}} \cdot Q_{\text{rot}}^{\text{D}}}{Q_{\text{trans}}^{\text{L}} \cdot Q_{\text{vib}}^{\text{L}} \cdot Q_{\text{rot}}^{\text{L}}} \exp(-\Delta_r H_0^0/RT)$$

where R is the gas constant and $\Delta_r H_0^0$ denotes the enthalpy of reaction for the stereomutation at 0 K: $\text{D} \rightleftharpoons \text{L}$. It is related to $\Delta_{\text{pv}} E$ by $\Delta_r H_0^0/N_A = \Delta_{\text{pv}} E + (E_Z^{\text{D}} - E_Z^{\text{L}})$ and the zero point energy E_Z in the harmonic approximation includes the parity-violating contribution:

$$E_Z^{\text{(D,L)}} = \frac{1}{2} \sum_{j=1}^{3N-6} k \theta_{\text{vib}}^{\text{(D,L)}}(j)$$

The translational partition function does not depend on the parity-violating potential, which is neglected here. Thus,

$$k(T) \approx \frac{\prod_{X=A,B,C} (1 - \Delta \theta_{\text{rotX}}^0 / 2 \theta_{\text{rotX}}^0)}{\prod_{X=A,B,C} (1 + \Delta \theta_{\text{rotX}}^0 / 2 \theta_{\text{rotX}}^0)} \cdot \frac{\prod_{j=1}^{3N-6} (1 + \Delta \theta_{\text{vib}}(j) Q_{\text{vib}}^0(j-1)/T)}{\prod_{j=1}^{3N-6} (1 - \Delta \theta_{\text{vib}}(j) Q_{\text{vib}}^0(j-1)/T)} \cdot \exp(-\Delta_r H_0^0/RT)$$

In the linear approximation, it can be written for small numbers $b_k (b_k \ll 1)$

$$\prod_k (1 - b_k) \approx 1 - \sum_k b_k$$

Then $K(T)$ is finally obtained. Let

$$x = - \left[\sum_{X=A,B,C} \frac{\Delta \theta_{\text{rotX}}^0}{\theta_{\text{rotX}}^0} + 2 \sum_{j=1}^{3N-6} \frac{\Delta \theta_{\text{vib}}(j)}{T} (Q_{\text{vib}}^0(j) - 1) \right]$$

$$y = - \frac{\Delta_r H_0^0}{RT}$$

$$K(T) \approx (1+x) \cdot (1+y) = 1+x+y+xy,$$

When $x \ll 1$ then $\exp x \approx 1+x$,

$$K \approx 1 - \frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\Delta S/R = x + xy = x(1+y) \approx x$$

Since the thermodynamic state functions are related to the total partition function, the influence of the parity-violating potential on the state functions is determined. Quack^[37] presented x

Table 1 x and y parameters for CDBrCIF^[37]

	300 K		4 K	
	$10^{17}x$	$10^{15}y$	$10^{17}x$	$10^{15}y$
CDBrCIF ^a	+5.035451	-8.503477	-3.029760	-6.377608
CDBrCIF ^b	+6.225475	-8.503477	-3.029760	-6.377608

a) results obtained in the separable harmonic adiabatic approximation (SHAA),

b) results obtained in the separable anharmonic adiabatic approximation (SAAA)

and y parameters for CDBrCIF at a temperature of 300 K and 4 K. The racemization reaction is $\text{L-CDBrCIF} \rightleftharpoons \text{D-CDBrCIF}$. Wang *et al.* calculated the macroscopic properties—the enthalpy $\Delta_r H_0^0$ and the entropy $\Delta_r S$ of (D, L)-CDBrCIF from x and y data of Quack & Stohner (Table 1, 2)

After we advance the concept of parity-violating entropy differences ($\Delta_r S^0$) and calculate Quack's values both in 300 K and 4 K, we can easily find that their signs change from positive (300 K) to negative (4 K). The sign reversal of $\Delta_r S^0$ should be considered as an experimental fact, which should be stressed much importance on. The $\Delta_r H_0^0$ effect is about five orders of magnitude larger than that of $\Delta_r S^0$, we believe that the above special physical phenomenon should have its significant consequences. Since translational partition function does not depend on the parity-violating potential, we can deduce that

$$\Delta_r S = S_{\text{vib}}^{\text{D}} + S_{\text{rot}}^{\text{D}} - S_{\text{vib}}^{\text{L}} - S_{\text{rot}}^{\text{L}}$$

$$\Delta_r S = \Delta S_{\text{vib}}^{\text{D-L}} + \Delta S_{\text{rot}}^{\text{D-L}}$$

Because molecular spectra can satisfactorily unravel the rotational and vibrational information of molecules, we perform the following temperature-dependent polarized Raman spectroscopy of D- and L-alanine single crystals.

2 Temperature-dependent Raman spectroscopy

D-, L- and DL- alanines (Sigma Chemical Cooperation) were purified by recrystallization from saturated aqueous solutions, respectively. The alanine single crystals were grown by slow evaporation 2~3 weeks at 277 K (Evaporation times of less than one week increased the inhomogeneous contribution to the phonon line shapes^[38]), washed with absolute alcohol, producing well-formed crystal elongated along the c axis, evacuated and

Table 2 $\Delta_r H_0^0$, $\Delta_r S$ and $\Delta_r G$ for CDBrCIF^[37]

	300 K			4 K		
	$10^{11} \Delta_r H_0^0$ J·mol ⁻¹	$10^{16} \Delta_r S$ J·K ⁻¹ ·mol ⁻¹	$10^{11} \Delta_r G$ J·mol ⁻¹	$10^{11} \Delta_r H_0^0$ J·mol ⁻¹	$10^{16} \Delta_r S$ J·K ⁻¹ ·mol ⁻¹	$10^{11} \Delta_r G$ J·mol ⁻¹
CDBrCIF ^a	+2.1209372	4.1864739	+2.1083778	+2.1209373	-2.5189424	+2.121038
CDBrCIF ^b	+2.1209372	5.1758599	+2.1054097	+2.1209373	-2.5189424	+2.121038
	$\Delta_r H > 0$	$\Delta_r S > 0$	$\Delta_r G > 0$	$\Delta_r H > 0$	$\Delta_r S < 0$	$\Delta_r G > 0$

a, b are the same as Table 1.

kept in a desiccator. The purity of the sample was characterized by elemental analysis (C, H, and N) and X-ray diffraction crystallography^[27-31]. Atomic force microscopy was used to characterize the surface of D- and L-alanine crystals without defects or micro bubbles^[39-40]. The rotation angle of the D- and L-alanine aqueous solution was measured on Polarimeter PE-241 MC at 293 K with wavelength 589.6 nm by using $[\alpha]_D^{293\text{K}} = -1.76^\circ$ (D) and 1.78° (L), respectively^[27].

Polarized Raman spectroscopy has been performed to probe the phase transition of organic crystals^[41]. Vibration spectra of DL-, D- and L- alanine crystals were performed on a Renishaw system 1000 fitted with argon-ion laser model. The temperature was monitored from 290 to 230 K by a digital temperature controller unit having a stability of 0.1 K. The laser beam propagated along the *c* axis perpendicular to the (110) face, which indexed using X-ray measurements. The experimental conditions were as follows: exciting line 514.5 nm, power 50 mW; the slit width 50 μm ; scanning range 100~3600 cm^{-1} ; signal averaging 3 scans.

In solid state Raman spectra, the methyne ($\text{C}_\alpha\text{—H}$) and symmetric methyl (CH_3) stretching peaks are close to each other and are nearly superimposed in the parent molecule of alanine. The relatively intense peak at ca. 2890 cm^{-1} , present in all species containing a CH_3 , is attributed to a Fermi resonance enhanced overtone of the methyl deformations at ca. 1461 cm^{-1} . A second overtone band centered at 2967 cm^{-1} was the methyne ($\text{C}_\alpha\text{—H}$) and symmetric methyl stretching peaks superimposed. In the experiment, the temperature-dependent relative intensity of $I(3000\text{ cm}^{-1})/I(2967\text{ cm}^{-1})$ in D- and L-alanine crystals clearly shows the existence of a phase transition around 258 K (Fig.2). The other important result is the apparent different Raman spectra of DL-alanine crystal when the temperature approaches the

critical temperature (250 K). A careful observation of this phase transition showed that^[41-42]: (1) the relative peak intensity of 1483 cm^{-1} ($\text{C}_\alpha\text{—H}$ bending) is stronger than that of 1411 cm^{-1} peak (COO^- symmetric bending) at 250 K, which represents the contribution of $\text{C}_\alpha\text{—H}$ bond and COO^- group to the phase transition of DL-alanine; (2) the relative intensity of 2953 cm^{-1} ($\text{C}_\alpha\text{—H}$ stretching vibration) is stronger than that of 3002 cm^{-1} (methyl symmetric vibration) at 250 K. These phenomena imply the abrupt change of vibration particulars of $\text{C}_\alpha\text{—H}$ bond at the transition temperature (~250 K), which agreed with the temperature-dependent neutron diffraction data^[43-44]. It provides insight into the dynamics of the molecular vibration, in which the spectroscopic behaviors of D- and L-alanine become very different even contrary. This evidence hints an underling relation between this spectroscopic abnormality and the sign reversal of parity-violating entropy difference.

3 The effect of temperature on parity-violating energy difference(PVED)

In 2000, Berger *et al.*^[45] and Laerdahl *et al.*^[46] concurrently concluded that, in addition to parity-violating potentials being frequently at least an order of magnitude larger than previously calculated, earlier conclusions on the PVEDs of amino acids and sugars were uncertain even with respect to the sign due to the complexity and flexibility of the accessible molecular conformations. The results of Berger *et al.* showed that PVED near the minimized geometry is relatively small and can sharply change its sign at thermal energies. They showed that while all values of dihedral angle α correspond to the L-alanine, the sign of ΔE_{PV} changes repeatedly from negative (L-alanine is more stable than D-alanine) to positive values through the range between 0 and 180° . Meanwhile, calculating PVEDs for the thirteen stable conformers of gaseous alanine by Laerdahl *et al.*, indicated that the stabilization of a certain enantiomer is strongly dependent on its flexible and highly dynamic structure of the biomolecule and unknown effects of its environment (naturally occurring L-alanine is preferred for only seven of the thirteen investigated structures), which allows no definite conclusion on the relative stability of the two chiral forms to explain the origin of homochirality in living organisms.

The remarkable sensitivity of PVED was confirmed in relation to the biomolecular conformation by Kitayama *et al.*^[47]. In the case of amino acids, Kikuchi *et al.*^[48] obtained a two-dimen-

Fig.2 Relative intensity of $I(3000\text{ cm}^{-1})/I(2967\text{ cm}^{-1})$ in D- and L-alanine

sion PVEDs energy map of L-alanine zwitterions in aqueous solution as a function of the $\text{NH}_3(\phi)$ and $\text{CO}_2(\theta)$ torsional angles, with comparable sizes of negative areas and positive ones. As for the dynamic parity violation, Kikuchi *et al.* calculated the PVEDs at the transition state and suggested that L-enantiomer is less preferable to D-enantiomer in Strecker synthesis of alanine^[49], which challenges the previously considered significance of kinetic effects in the formation of homochirality^[50].

The structure of L- and D-alanine has been determined with X-ray crystallography. The unit cell dimensions and cell parameter of L- and D-alanine were collected on a Rikagu RAXIS-RAPID imaging plate diffractometer with graphite monochromated Mo- K_α radiation($\lambda=0.071069$ nm) at 300, 270 and 250 K^[28,44]. From the X-ray data, the CO_2 torsion angles θ of L-alanine are calculated to be -19.18° , -19.11° and -19.04° , and the ϕ of NH_3 torsion angles almost equal to 76.8° at 300, 270 and 250 K, respectively. According to the dihedral angles of L-alanine, 44.21° , 45.20° and 45.72° obtained through X-ray diffraction and molecular conformation calculation, we can deduce from the two-dimension PVEDs energy map from Berger^[45] and Kikuchi^[48] that, the PVEDs of condensed-phase alanine molecule in ordinary temperatures (250~300 K) quite approach zero.

In short, although we cannot make sure the exact absolute values of temperature-dependent PVEDs because of the limitation of computation accuracy, it is quite reasonable for us to propose that for alanine crystals there should exist a critical temperature at which the conformational dependent PVED is zero. In the following, we will hypothetically discuss the possible observably physical consequences of molecular parity violation vanishing in condensed phase.

4 Spontaneous symmetry breaking

The secret of nature is symmetry, but much of the texture of the world is due to mechanisms of symmetry breaking. There are a variety of mechanisms wherein the symmetry in nature can be hidden or broken. A more profound way of hiding symmetry is the phenomenon of spontaneous symmetry breaking. The laws of physics are symmetric but the state of the system is not. In systems with an infinite number of degrees of freedom, however, global symmetries may be realized in two different ways. The first way is standard: the laws of physics are invariant and the ground state of the theory is unique and symmetric, as is the case for quantum mechanical systems with a finite number of degrees

of freedom. However in systems with an infinite number of degrees of freedom a second mode is possible, in which the ground state is asymmetric. Such spontaneous symmetry breaking is responsible for the existence of crystals (that break translational invariance), magnetism (in which rotational invariance is broken), superconductivity (in which the phase invariance of charged particles is broken), and the structure of the unified electroweak theory.

Associated with spontaneous symmetry breaking is the phenomenon of symmetry restoration. If one heats a system that possesses a broken symmetry, it tends to be restored at high temperature. Thus a ferromagnetic material can be magnetized at low temperature with all the little atomic magnets aligned in the same direction. This is a state of broken rotational symmetry. As the temperature increases, the atoms vibrate more and more. Finally when the temperature is greater than a certain critical value, the fluctuations overcome the forces that tend to align the atomic magnets and the average magnetization vanishes. Above the critical temperature the system exhibits rotational symmetry. Such a transition from a state of broken symmetry to one where the symmetry is restored, is a phase transition. We believe that the same phenomenon occurs in the case of the symmetries of the fundamental forces in nature. Many of these are broken at low temperatures. Very early in the history of the universe, when the temperature was very high, all of these symmetries in nature were presumably restored. The resulting phase transitions, as the universe expanded and cooled, from symmetric states to those of broken symmetry have important cosmological implications.

5 ^1H CRAMPS solid state NMR spectra of D-/L-alanine

The ^1H CRAMPS ssNMR spectra were run on a Varian InfinityPlus-400 spectrometer with resonance frequencies 400.12 MHz ^1H of D- and L-alanine. For the sake of investigating the temperature dependent proton nucleus dynamics of D- and L-alanine molecules, the chemical shifts and peak widths of $\alpha\text{-H}$ and $\beta\text{-H}$ of D- and L- alanines were measured. Fig.3 displays that four peak's widths of $\alpha\text{-H}$ and $\beta\text{-H}$ experience distinct maximum around 240 K. So we conjecture that both D- and L-alanines may undergo a phase transition in this temperature range. The peak linewidth represents spin-spin relaxation times half height linewidth is given by $\Delta_{1/2}=1/\pi T_2$. $R_2=1/T_2$ is the sum of several contributions, which corresponding to the different

Fig.3 Temperature dependence of peak widths of α -H, β -H of D- and L-alanine

mechanisms, namely quadrupolar R_2^Q , dipolar interaction R_2^D , chemical shift anisotropy R_2^{CSA} and spin-spin coupling (J-coupling) R_2^J . In the CRAMPS experiment, the dipolar interaction R_2^D and the chemical shift anisotropy R_2^{CSA} are averaged out to zero. By choosing a spin 1/2 nucleus (^1H), the nuclear quadrupole moment is equal to zero, thus R_2^Q cancels out. The J-coupling R_2^J might be the predominant contribution. This part of study indicates the obvious difference of J-coupling R_2^J values between D- and L-alanines in the phase transition process.

The most striking point of these results is that the relative differences of J-coupling R_2^J values between D- and L- alanines are much larger at the critical temperature than those in the nearby temperatures, which is well compatible with our theoretical assumption that the enantiomer difference is amplified when the PVED approaches zero at the critical temperature. In D- and L-alanine case, the half height linewidth $\Delta_{1/2}$ is determined by the spin-spin relaxation time T_2 . T_2 is the interaction time constant. $\Delta_{1/2} = 1/\pi T_2$. The peak linewidth of NMR spectra is originated from the uncertainty principle: $\Delta E \times \Delta t \approx h$. Here, Δt is the time of the particle staying on a certain energy state. In the NMR phenomena, the staying time of nuclear magnetic moment Δt is decided by spin-spin interaction, therefore: $\Delta E \cdot T_2 \approx h$, $\Delta E = h\Delta\nu$, $\therefore \Delta\nu \approx 1/T_2$. Because of the inhomogeneous of the magnetic field $\therefore \Delta\nu \approx 1/T_2'$, T_2' is the apparent transverse relaxation time $\therefore \Delta_{1/2} \approx 1/\pi T_2'$.

Therefore,

$$\Delta E_D = h\Delta\nu_D \approx h \times 1/T_{2,D}' \approx 5.226 \times 10^{-12} \text{ (eV)}$$

$$\Delta\nu_D \approx 1.263 \text{ kHz}$$

$$\Delta E_L = h\Delta\nu_L \approx h \times 1/T_{2,L}' \approx 3.299 \times 10^{-12} \text{ (eV)}$$

$$\Delta\nu_L \approx 0.798 \text{ kHz}$$

Calculations of the PVED between mirror image molecules have been reported for light molecules^[50-51] and lie in the range $10^{-15} \sim 10^{-20}$ eV. The effect of the PNC contribution to the spin-spin coupling between electrons S_1DS_2 in the triplet state of chiral molecules has been considered. $\Delta E \approx 10^{-12} \sim 10^{-13}$ eV with respect to the spin-orbit coupling has been estimated^[52].

In summary, molecular parity violation arises like a contact interaction between electron and nucleons (in practice the nucleus) because of the short range of the weak nuclear interaction mediated by the massive Z boson as a field particle. This can be related to the gradient of the wave-function of the electron at the position of the nucleus, which is comparable (but not identical) to the Fermi contact interaction which is responsible for the hyperfine structure in the J-coupling constants in NMR spectra.

6 Tunneling dynamics of amino acid

In 2004, Lee *et al.*^[53] suggested a model for chiral evolution on the quantum tunneling dynamics in double well potentials for the inversion of an amino acid. They introduce an asymmetric double-well potential with a subtle difference in the depths of the potential wells, which represents the presence of PVED between two optical isomers^[54]. Our experimental results support Salam prediction^[55-58] of second-order phase transition involving dynamic symmetry breaking as an amplification mechanism, which plays a bifurcation-type in amino acids. In the kinetic model, there exists an induction period (temperature-induced phase transitions) before bifurcation point, where the amounts of the two enantiomers are equal. Tunneling dynamics through asymmetric double-well with PVED results in disproportion of optical isomers, can lead to the enrichment of one of the enantiomers such as L-amino acid. It is suggested that tunneling dynamics of amino acids with PVED provides a plausible mechanism for much faster development of homochirality.

7 Conclusion and outlook

The weak neutral currents are a central prediction of the unified theory of weak and electromagnetic forces developed by Glashow and Weinberg^[59-60]. The important tests of the theory have been to find the expected effects of the neutral current interaction in atoms such as Cs^[61], Bi^[62], and Tl^[63]. These results demonstrate that parity conservation is violated in atoms at the level predicted by the Weinberg-Salam theory. In molecular physics, the situation is quite different. Because the PVED

scales to the fifth power of the nuclear charge of the heaviest atom in the molecule, a few researchers synthesized compounds containing heavy elements^[22, 64]. However, the role of chirality in the theories that determine the origin of life, remains a mystery and is a subject of intense debate^[3, 65]. Parity violation energy due to weak nuclear interaction between nucleons and electrons in chiral amino acid molecules provides a fundamental tool to verify our understanding of electronic behavior in living systems.

The temperature effects on the parity-violating entropy and energy differences are significant and can have many remarkable implications; the temperature-dependent polarized Raman spectra of D- and L-alanine single crystals revealed the possible occurrence of sign reversal of $\Delta_r S^0$ of alanine at a critical temperature. The present result will be the spectroscopic evidence of the temperature effect on the $\Delta_r S^0$ of enantiomers.

The temperature effect on PVED, showing simultaneous vanishing of molecular parity violation in condensed-phase amino acids, plays a central role in the spontaneous symmetry breaking. Such a hypothesis is well compatible with the kinetic model, there exists an "induction period" before bifurcation point, where the amounts of the two enantiomers are equal. Tunneling dynamics through asymmetric double-well with PVED results in disproportion of optical isomers even at short-time scales. Such initial disproportion can be quickly amplified by competitive autocatalysis reactions. It can be argued that tunneling dynamics of amino acids with PVED provides a plausible mechanism for accelerated chiral evolution.

The significance of the present study on the molecular physics may be the most profound. However, the arguments between scientists are the purity of the D-, L- and DL- crystals and the experimental results can be valid in different laboratories. Manuel *et al.*^[66] reported the standard molar enthalpies of formation of crystalline D-, L- and DL- valines at 298 K, as $-(612.9 \pm 1.5)$, $-(614.7 \pm 1.3)$, and $-(617.1 \pm 1.0)$ $\text{kJ} \cdot \text{mol}^{-1}$ respectively. Kamaguchi *et al.*^[67] measured the enthalpies of combustion of twice, twice and four times recrystalliation of D-, L-, and DL-alanines at 298.15 K are as follows: $\Delta E_c^0 = -(1619.24 \pm 0.58)$, $-(1620.26 \pm 0.63)$ and $-(1617.97 \pm 0.50)$ $\text{kJ} \cdot \text{mol}^{-1}$, $\Delta H_f^0 = -(561.08 \pm 0.71)$, $-(560.06 \pm 0.76)$ and $-(562.35 \pm 0.65)$ $\text{kJ} \cdot \text{mol}^{-1}$, respectively. ΔH_f^0 ((D-L) valine) = $1.8 \text{ kJ} \cdot \text{mol}^{-1} = 1.9 \times 10^{-2} \text{ eV}$, ΔH_f^0 ((D-L) alanine) = $1.02 \text{ kJ} \cdot \text{mol}^{-1} = 1.1 \times 10^{-2} \text{ eV}$. The difference of standard molar formation enthalpies of valine enantiomers is

about two-fold larger than alanine enantiomers. The theoretical PVED value of (D-L) valine ($6.2 \times 10^{-19} \text{ eV}$) is also two-fold larger than that of (D-L) alanine ($3.0 \times 10^{-19} \text{ eV}$) by Tranter *et al.*^[68-69].

We used specific heat measuring methods on DSC with a twin sample (D- and L-valine) employed in an adiabatic differential calorimeter. In order to maintain zero temperature difference between the twin samples, the system was operated by continuous heating power controlled by computer, independently. We found the ΔE_{PV} value of valine enantiomer $\Delta E_{PV} = E_{PV,D} - E_{PV,L} = 2E_{PV,D}$, $\Delta C_p = d\Delta E_{PV}/dT = 0.627 \text{ J} \cdot \text{mol}^{-1} = 6.5 \times 10^{-6} \text{ eV} \cdot \text{K}^{-1}$ at the phase transition temperature, which is 10^{12} times higher than the theoretical value. However, $d\Delta E_{PV}/dT$ was reflected in the slope difference of two $\Delta C_p - T$ curves of D- and L-valine when phase transition occurred. Based on the ^1H -MAS and CRAMPS ssNMR spectra, we conjectured that the electron spin of $\alpha\text{-H}$ in D-valine (alanine) causes a flip at T_c by decreasing the hydrogen atom's total spin from one to zero then released the energy $6 \times 10^{-6} \text{ eV}^{[70-71]}$, which coincides with the measured energy difference in λ peak of second-order phase transition of (D-L) valine^[28]. Recently, Rakvin *et al.*^[72] have carried out heat capacity (C_p) and electron spin echo measurements on L-alanine. The obtained C_p data show the Boson peak (a maximum in C_p/T^3 versus T plots) in the low temperature region (1.8~20 K), which confirm the existence of a thermally activated dynamic orientational disorder in the lattices and also provide a mechanism for the spin-lattice relaxation at cryogenic temperature.

The experimental and theoretical progresses provided an impetus to many physicists and chemists to propose and attempt numerous strategies to search for the tiny parity violating effects in the field of molecular physics. It is somewhat surprising that recent articles and reviews dealing with the physical basis of the origin of molecular parity violation pay little attention to the temperature effects. Perhaps one may naively take a point of view that temperature cannot bring any observable consequences to this already quite minute effect. Consequently, it can be said that explorations would relate to fundamental aspects of our understanding of the world, in particular in relation to the underlying symmetries of physical laws^[73], from left-right asymmetry at the level of elementary particles to the cosmic preference of matter over antimatter^[74].

Acknowledgments We acknowledge professor Xinsheng Zhao for helpful discussions and support of Renishaw system 1000 instrument.

We are grateful to Dr. Jianhua Ouyang for technical assistance in Raman spectroscopy measurements.

References

- 1 Quack, M. *Angew. Chem. Int. Ed.*, **1989**, **28**:571
- 2 Bonner, W. A. *Orig. Life Evol. Biosphere.*, **1991**, **21**:59; **1995**, **25**:175
- 3 Avetisov, V.; Goldanskii, V. *Proc. Natl. Acad. Sci. USA*, **1996**, **93**:11435
- 4 Avalos, M.; Babiano, R.; Cintas, P.; Jimenez, J. L.; Palacios, J. C. *Chem. Commun.*, **2000**, **11**:887; *Tetrahedron:Asymmetry*, **2000**, **11**:2845
- 5 Buschmann, H.; Thede, R.; Heller, D. *Angew. Chem. Int. Ed.*, **2000**, **39**:4033
- 6 Bonner, W. A. *Chirality*, **2000**, **12**:114
- 7 Podlech, J. *Cell. Mol. Life Sci.*, **2001**, **58**:44
- 8 Cintas, P. *ChemPhysChem*, **2001**, **2**:409
- 9 Cintas, P. *Angew. Chem. Int. Ed.*, **2002**, **41**:1139
- 10 Quack, M. *Angew. Chem. Int. Ed.*, **2002**, **41**:4618
- 11 Compton, R. N.; Pagni, R. M. *Adv. Atom. Mol. Opt. Phys.*, **2002**, **48**:219
- 12 van't Hoff, J. H. Die lagerung der atome im raume. Braunschweig: Vieweg, 1876
- 13 Lee, T. D.; Yang, C. N. *Phys. Rev.*, **1956**, **104**:254
- 14 Wu, C. S.; Amber, E.; Hayward, R. W.; Hoppes, D. D.; Hudson, R. *Phys. Rev.*, **1957**, **105**:1413
- 15 Rein, D. *J. Mol. Evol.*, **1974**, **4**:15
- 16 Letokhov, V. *Phys. Lett. A*, **1975**, **53**:275
- 17 Hund, F. *Z. Physik.*, **1927**, **43**:805
- 18 Avalos, M.; Babiano, R.; Cintas, P.; Jimenez, J. L.; Palacios, J. C.; Barron, L. D. *Chem. Rev.*, **1998**, **98**:2391
- 19 Zanasi, R.; Lazzeretti, P. *Chem. Phys. Lett.*, **1998**, **286**:240; Zanasi, R.; Lazzeretti, P.; Ligabue, A.; Soncini, A. *Phys. Rev. E*, **1999**, **59**:3382
- 20 Daussey, C.; Marrel, T.; Amy-Klein, A.; Nguyen, C. T.; Borde, C. J.; Chardonnet, C. *Phys. Rev. Lett.*, **1999**, **83**:1554
- 21 Ziskind, M.; Daussey, C.; Marrel, T.; Chardonnet, C. *Eur. Phys. J. D*, **2002**, **20**:219
- 22 Lahamer, A. S.; Mahurin, S. M.; Compton, R. N.; House, D.; Laerdahl, J. K.; Lein, M.; Schwerdtfeger, P. *Phys. Rev. Lett.*, **2000**, **85**:4470
- 23 Pagni, M.; Compton, R. N. *Cryst. Growth Des.*, **2002**, **2**:249
- 24 Harris, R. A.; Stodolsky, L. *Phys. Lett.*, **1978**, **18B**:313.
- 25 Harris, R. A. *Chem. Phys. Lett.*, **2002**, **365**:343
- 26 Schwerdtfeger, P.; Gierlich, J.; Bollwein, T. *Angew. Chem. Int. Ed.*, **2003**, **42**:1293
- 27 Wang, W. Q.; Yi, F.; Ni, Y. M.; Zhao, Z. X.; Jin, X. L.; Tang, Y. Q. *J. Biol. Phys.*, **2000**, **26**:51
- 28 Wang, W. Q.; Liang, Z. *Acta Phys.-Chim. Sin.*, **2001**, **17**(12):1077 [王文清, 梁 智. 物理化学学报(*Wuli Huaxue Xuebao*), **2001**, **17**(12):1077]
- 29 Wang, W. Q.; Min, W.; Bai, F.; Sun, L.; Yi, F.; Wang, Z. M.; Yan, C. H.; Ni, Y. M.; Zhao, Z. X. *Tetrahedron:Asymmetry*, **2002**, **13**:2427
- 30 Wang, W. Q.; Min, W.; Liang, Z.; Wang, L. Y.; Chen, L.; Deng, F. *Biophys. Chem.*, **2003**, **103**:289; **2003**, **106**:96
- 31 Wang, W. Q.; Min, W.; Zhu, C. F.; Yi, F. *Phys. Chem. Chem. Phys.*, **2003**, **5**:4000
- 32 Barthes, M.; Bordallo, H. N.; Denoyer, F.; Lorenzo, J. E.; Zaccaro, J.; Robert, A.; Zontone, F. *Eur. Phys. J. B*, **2004**, **37**:375
- 33 Sullivan, R.; Pyda, M.; Pak, J.; Wunderlich, B.; Thompson, J. R.; Pagni, R.; Pan, H.; Barnes, C.; Schwerdtfeger, P.; Compton, R. N. *J. Phys. Chem. A*, **2003**, **107**:6674
- 34 Wang, W. Q.; Sheng, X. R.; Yang, H. S.; Zhuang, Z. Z.; Chen, Z. *J. Biol. Phys.*, **1994**, **20**:247
- 35 Robert, J. B.; Barra, A. L. *Chirality*, **2001**, **13**:699
- 36 Faglioni, F.; Lazzeretti, P. *Phys. Rev. A*, **2003**, **67**:1
- 37 Quack, M.; Stohner, J. *Chirality*, **2001**, **13**:745; **2003**, **15**:375
- 38 Crowell, R. A.; Chronister, E. L. *Phys. Rev. B*, **1993**, **48**(1):172
- 39 Wang, W. Q.; Gong, Y.; Liang, Z.; Sun, F. L.; Shi, D. X.; Gao, H. J.; Lin, X.; Jiang, P.; Wang, Z. M. *Surf. Sci.*, **2002**, **512**:L379
- 40 Gong, H. M.; Liu, H. W.; Wang, Y. L.; Gao, H. J.; Gong, Y.; Jiang, H. Y.; Wang, W. Q. *Surf. Sci.*, **2004**, **552**:70
- 41 Lima, R. J. C.; Freire, P. T. C.; Sasaki, J. M.; Melo, F. E. A.; Mendes, F. J.; Moreira, R. *J. Raman Spectrosc.*, **2001**, **32**:751
- 42 Wang, C. H.; Storms, R. D. *J. Chem. Phys.*, **1971**, **55**:3291
- 43 Wang, W. Q.; Liu Y. N.; Gong, Y. *Acta Phys.-Chim. Sin.*, **2004**, **20**(11):1345 [王文清, 刘轶男, 龚 葵. 物理化学学报(*Wuli Huaxue Xuebao*), **2004**, **20**(11):1345]
- 44 Wang, W. Q.; Gong, Y.; Yao, N. *Acta Phys.-Chim. Sin.*, **2005**, **21**(7):774 [王文清, 龚 葵, 姚 楠. 物理化学学报(*Wuli Huaxue Xuebao*), **2005**, **21**(7):774]
- 45 Berger, R.; Quack, M. *ChemPhysChem*, **2000**, **1**:57
- 46 Laerdahl, J. K.; Wesendrup, R.; Schwerdtfeger, P. *ChemPhysChem*, **2000**, **1**:60
- 47 Kitayama, T.; Ushikubo, T.; Morihashi, K.; Kikuchi, O. *J. Mol.*

- Struct. (Theochem.)*, **2002**, **586**: 1
- 48 Kitayama, T.; Kiyonaga, H.; Morihashi, K.; Takahashi, O.; Kikuchi, O. *J. Mol. Struct. (Theochem.)*, **2002**, **589-590**: 183
- 49 Kitayama, T.; Watanabe, T.; Takahashi, O.; Morihashi, K.; Kikuchi, O. *J. Mol. Struct. (Theochem.)*, **2002**, **584**: 89
- 50 Rein, D. W.; Hegstrom, R. A.; Sandars, P. G. H. *Phys. Lett. A*, **1979**, **71**: 499
- 51 Hegstrom, R. A.; Rein, D. W.; Sandars, P. G. H. *J. Chem. Phys.*, **1980**, **73**: 2329
- 52 Harris, R. A.; Stodosky, L. J. *J. Chem. Phys.*, **1980**, **73**: 3862
- 53 Lee, K.; Shin, S.; Ka, J. *J. Mol. Struct. (Theochem.)*, **2004**, **679**: 59
- 54 Janoschek, R. in: Janoschek, R. (Ed.), *Chirality: from weak bosons to the α -helix*. Berlin: Springer, 1991: 18
- 55 Salam, A. *Phys. Lett. B*, **1992**, **288**: 153
- 56 Salam, A. *J. Mol. Evol.*, **1991**, **33**: 105
- 57 Salam, A. *Chemical evolution: origin of life*. Hampton Virginia of USA: Deepak Publishing, 1993: 101
- 58 Wang, W. Q.; Yao, N.; Chen, Y.; Lai, P. *Life in the Universe*. Seckbach, J. *et al.* eds. Netherlands: Kluwer Academic Publishers, 2004: 79
- 59 Glashow, S. L. *Nucl. Phys.*, **1961**, **22**: 579
- 60 Weinberg, S. *Phys. Rev. Lett.*, **1967**, **19**: 1264
- 61 Bouchiat, M. A.; Bouchiat, C. C. *Phys. Lett. B*, **1974**, **48**: 111
- 62 Sore, D. C.; Fortson, E. N. *Bull. Am. Phys. Soc.*, **1975**, **20**: 491
- 63 Chu, S.; Conti, R.; Commins, E. D. *Phys. Lett. A*, **1977**, **60**: 96
- 64 Szabo-Nagy, A.; Keszthelyi, L. *Proc. Natl. Acad. Sci. USA*, **1999**, **96**: 4252
- 65 Hegstrom, R. A.; Kondepudi, D. K. *Scientific American*, **1992**: 98
- 66 da Silva, M. A. V. R.; da Silva, M. D. M. C. R.; Santos, L. M. N. B. F. *J. Chem. Thermodynamics*, **2000**, **32**: 1037
- 67 Kamaguchi, A.; Sato, T.; Sato, M.; Sakiyama, M.; Seki, S. *Bulletin of the Chemical Society of Japan*, **1975**, **48**(12): 3749
- 68 Mason, S. F.; Tranter, G. E. *Proc. R. Soc. Lond.*, **1985**, **A397**: 45
- 69 Tranter, G. E.; MacDermott, A. *J. Croatica Chem. Acta*, **1989**, **62**(2A): 165
- 70 Rith, K.; Schäfer, A. *Scientific American*, **1999**: 58
- 71 Wang, W. Q.; Gong, Y.; Li, C. *Chinese Science Bulletin*, **2002**, **47**(7): 603
- 72 Rakvin, B.; Maltar-Strmeäki, N.; Ramsey, C. M.; Dalal, N. S. *J. Chem. Phys.*, **2004**, **120**: 6665
- 73 Kosso, P. *Stud. Hist. Phil. Sci.*, **1999**, **30**(3): 479
- 74 Avalos, M.; Babiano, R.; Cintas, P.; Jimenez, J. L.; Palacios, J. C. *ChemPhysChem*, **2003**, **3**: 1001

手性氨基酸分子的温度诱导相变——自发对称性破缺与复原*

王文清 闵 玮 龚 葵

(北京大学化学与分子工程学院应用化学系, 北京 100871)

摘要 运用统计理论热力学函数自由能 ΔG 、焓 ΔH 、熵 ΔS 、平衡常数 K 与粒子平动、振动、转动配分函数关系, 并通过变温 D- 与 L-CDBrCIF 实例计算, 证明在宏观温度变量下, 可以导致手性分子 $D \rightleftharpoons L$ 平衡中宇称破缺熵差的反号. 根据作者科研组 14 年来, 采用变温 X 衍射、中子衍射、比热、直流和交流磁化率、 ^1H 和 ^{13}C 固相核磁共振、拉曼光谱、晶体旋光和双折射、超声测定相变等实验方法, 证明 Salam 假说预言的温度范围 (200~250 K) 存在温度变量诱导的相变, 产生自发对称性破缺. 在宇称破缺能差(PVED)接近 0 条件下, 宇称破缺熵差导致 D 和 L 分子反向的物理行为, 产生分叉机制(bifurcation mechanism). D 和 L 分子的能量差别, 可能是早期生命起源时, L 氨基酸富集的原因. 实验还发现, 在低温变温下自发对称破缺的复原. 由于晶相结构限制分子重排, Salam 相变不是 $D \rightarrow L$ 的构型相变.

关键词: 温度效应, 温度-构象-宇称破缺能差关系, 宇称破缺熵差, 隧道动力学, 丙氨酸对映体
中图分类号: O641

2005-03-14 收到初稿, 2005-04-26 收到修改稿. 联系人: 王文清(Email: Wangwqchem@pku.edu.cn; Tel: 010-62752457). *国家自然科学基金(20452002)和国家科技部重大基础研究前沿专项(2004-36)资助项目