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High-level theoretical study of the evolution of abundances and interconversion of glycine conformers*

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The relative conformer energies of glycine are evaluated by using a focal point analysis expressed as (HF→MP2→MP3→CCSD→CCSD(T)). The conformer abundances at various temperatures (298–500 K) are calculated based on the relative energies and Boltzmann statistical thermostatistical analysis with and without considering internal hindered rotations. A comparison between the available Raman spectrum and the electron momentum spectrum confirms that the influence of rigid-rotor hindered rotation on the conformational proportions of glycine is considerable, especially for the IIIp structure. The conformational interconversions are discussed. It is found that with increasing temperature, the mole fraction of IIn keeps constant and Ip structure can convert into IVn and IIIp, leading to the decrease in the weight of Ip and the increase in the weights of IVn and IIIp conformers, which is in accordance with experimental observations.

Keywords: glycine, conformation, abundance, interconversion

PACS: 31.15.–p, 33.15.–e, 33.15.Bh, 31.15.xr **DOI:** 10.1088/1674-1056/27/4/043102

1. Introduction

As is well known, protein consists of amino acids. Glycine is the simplest in natural amino acids and is found in all body fluids and proteinaceous tissue, which serves as a prototype for larger or more complex amino acids or protein system. This compound is of fundamental biological interest and has been extensively studied as one of the cornerstones of molecular mechanics and conformational analysis.[1] Glycine is conformationally versatile due to the rotation about three intramolecular axes, i.e., N–C, C–C, and C–O bonds. Its potential energy surface is usually described[2] in terms of eight energy minima relating to the Ip, IIn, IVn, IIIp, Vn, VIp, VIIp, and VIIIn conformers (see Fig. 1). The experimental data about the conformational structure of glycine to date have covered the following aspects: the electron diffraction (ED) by Iijima *et al.*,[3] microwave (MW) studies,[4–9] He (II) photoelectron spectrum,[10] the (e, 2e) ionization spectrum at an impact electron energy of 1200 eV reported by Brion *et al.*,[11,12] infrared spectroscopic studies,[13,14] and raman spectrum.[15,16] So far, most high-level *ab initio* calculations performed for conformers of glycine have focused on the conformational geometric structures,[17–21] determination of conformational energy differences,[2,22–25] conformational relaxation,[26–28] and electron structure.[8,26,27] The various theoretical calculations predict that the two most stable glycine conformers are Ip and IIn. The evidence for the third conformation IVn and that for the fourth conformation IIIp are reported in Refs. [15] and [16]. In sharp contrast with the above-mentioned theoretical investigations, theoretical data about the statistical thermodynamics analysis, the effect of temperature on the conformer abundances, and conformational interconversion of eight free glycine conformers are relatively scarce. It should be noted that when studying molecules with conformational flexibility, such as amino acids, it is crucial to correctly estimate the conformational populations at various temperatures and cope with the influences of the various conformations on the experimental spectra, including Raman spectrum, PES spectrum, infrared spectrum, and electron momentum spectrum.[29–31] Recently, in Ref. [16], the inaccuracy of the rigid-rotor/harmonic-oscillator (RRHO) approximation to glycine conformations was experimentally confirmed, which indicates a more accurate study beyond the RRHO approximation on the conformer abundances of glycine is necessary.

The main purpose of the present investigation is to motivate the further conformational evolution with temperature and interconversion of conformationally versatile molecules, based on reliable enough theoretical grounds. Focal point analyses[32–34] at DFT (density functional theory) B3LYP/aug-cc-pVTZ geometries are carried out to evaluate the accurate relative conformer energies of glycine. Also, the values of relative Gibbs free energy ΔG at different temperatures are then calculated at the elementary rigid-rotor/harmonic-oscillator (RRHO) and rigid-rotor hindered rotation levels. Based on the extremely accurate relative energies, the abundances of rotamers of glycine in the gas phase, each as a function of temperature increasing from 298 K to 500 K, are evaluated. Finally, the possible transformation processes among various conformers at an experimental temperature of 438 K are discussed in detail.

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2. Methods and computational details

All calculated results are obtained based on the geometries of glycine conformers optimized at a DFT B3LYP/aug-cc-pVTZ theory level. A focal point analysis is used to estimate the relative energies of glycine conformers in the gas phase. Since the focal point analysis method is well documented in Refs. [32]–[34], we will summarize only the most important details of our computations here. The polarized valence basis sets of cc-pVDZ, cc-pVTZ, and cc-pVQZ are designated as cc-pVXZ, with X = D, T, and Q respectively. Well-suited extrapolations of the HF total electronic energies to complete basis set E_{∞}^{HF} for the neutral molecules and their cations can be obtained with a three-parameter exponential formula:[35]

$$E_l^{\mathrm{HF}} = E_{\infty}^{\mathrm{HF}} + A\,\mathrm{e}^{-Bl}, \tag{1}$$

where the cardinal number $l = 2,3,4,\ldots$ when X equals D, T, Q, …, respectively; A, B, and l are the parameters. In turn, the correlated total energies are extrapolated to an asymptotically complete basis set, indicated by E_{∞}, using a three-parameter extension of (named Schwartz 6(lmn)) Schwarz's extrapolation formula,[36] which is based on inverse powers of $(l+1/2)$:

$$E(l) = E_{\infty} + \frac{B}{(l+1/2)^4} + \frac{C}{(l+1/2)^6}. \tag{2}$$

Based on the accurate relative conformer energies of glycine, the relative abundance of each structure n_i is determined by means of Boltzmann statistical thermostatistical analysis, using the following expression:

$$n_i = \rho_i \exp(-\Delta G_i/RT). \tag{3}$$

Here, ρ_i is the symmetry number of species I; ΔG_i means the relative Gibbs free energy, which is obtained by considering the energy difference, zero-point vibrational energy correction, enthalpy correction, and entropy correction; R and T are the gas constant and temperature, respectively. Note that the thermochemical analysis for each species reported here goes beyond the RRHO approximation, because hindered rotations are included.

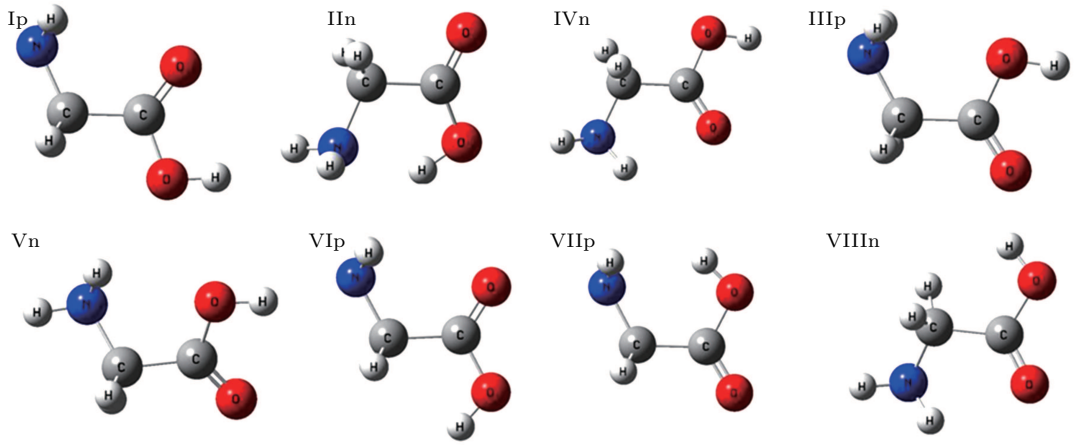


Fig. 1. (color online) Geometry structures of the eight conformers of glycine.

3. Results and discussion

3.1. Relative energies of glycine conformers

The eight conformers of glycine are optimized at the DFT B3LYP/aug-cc-pVTZ theory level as given in Fig. 1. Table 1 presents the calculated geometrical details, which are in good agreement with both experimental results given by electron diffraction measurements[3] and previous theoretical predictions.[18–21] The energies of glycine conformations relative to Ip (the most stable structure) derived from focal point analysis are shown in Table 2. All non italic energies in the table are calculated and the values displayed in boldface are our best estimates. Either the extrapolated energies to complete basis sets, or extrapolations derived from the corrections to relative energies of glycine conformations and best estimates are displayed in italic. The best estimates for the conformational energy differences between the given rotamer and rotamer Ip are shown at the lower right corner. Notice that the values in ΔHF entries are the relative energies of the given rotamer to rotamer Ip at the HF theory level, and the results shown in +MP2, +MP3, +CCSD, and +CCSD(T) entries correspond to the high-level correlation corrections to the lower-level relative conformer energies, being in the order of HF→MP2→MP3→CCSD→CCSD(T). For example, +MP2 (in the case of rotamer IIn) = [(HF total energy of rotamer Ip) – (HF total energy of rotamer IIn)] – [(MP2 total energy of rotamer Ip) – (MP2 total energy of rotamer IIn)] (i.e., the relative MP2 energy correction to the HF relative energy). Therefore, the sum of the values in a column up to a given row gives the relative energy of the given rotamer to rotamer Ip at a given level. For example, in the cc-pVDZ column of conformer IIn, ΔHF is the relative energy at the HF/cc-pVDZ level (13.835 kJ/mol). At the MP2/cc-pVDZ level the relative energy is the sum of ΔHF and +MP2 rows in the cc-pVDZ column ($13.835 - 12.412 = 1.423$ kJ/mol). At the CCSD/cc-pVDZ level the relative energy is the sum of ΔHF, +MP2, +MP3, and +CCSD rows in the cc-pVDZ column ($13.835 - 12.412 + 2.636 + 2.494 = 6.553$ kJ/mol).

Table 1. Selected geometric parameters of eight glycine conformers optimized at the B3LYP/aug-cc-pVTZ level.

Parameters	Ip	IIn	IVn	IIIp	Vn	VIp	VIIp	VIIIn
C–C	1.519	1.532	1.531	1.510	1.522	1.534	1.534	1.521
C–N	1.447	1.456	1.451	1.452	1.456	1.445	1.445	1.451
C–O	1.356	1.341	1.351	1.356	1.352	1.353	1.353	1.357
C=O	1.205	1.211	1.203	1.203	1.202	1.199	1.199	1.198
O–H	0.968	0.981	0.971	0.970	0.970	0.970	0.970	0.969
C–H	1.093	1.091	1.092	1.091	1.090	1.086	1.093	1.095
N–H	1.093	1.011	1.012	1.013	1.011	1.012	1.006	1.009
Θ(C,C,N)	115.52	111.93	110.51	119.43	113.45	115.78	119.17	111.30
Θ(C,C,O)	110.96	113.77	111.56	113.62	112.28	115.14	116.43	115.19
Θ(C,C=O)	125.62	122.46	125.84	123.57	125.00	124.45	122.31	124.28
Θ(C,O,H)	107.14	105.49	107.15	107.09	106.93	110.72	108.06	110.56
Θ(C,C,H)	107.42	107.32	105.16	106.14	105.34	108.00	106.22	106.11
Θ(C,N,H)	110.02	112.23	110.32	111.27	111.07	110.64	117.11	109.74
ψ(N,C,C,O)	180.00	–7.33	164.28	0.00	34.11	180.00	0.00	166.52
Ψ(C,C,O,H)	180.00	1.51	177.09	180.0	178.22	0.00	0.00	3.60

Table 2. Energies of glycine conformers relative to Ip derived from focal point analysis. Extrapolated energies are in italic (kJ/mol).

Rotamer	Basis	6-311G**[a]	cc-pVDZ[a]	aug-cc-pVDZ[a]	cc-pVTZ[a]	aug-cc-pVTZ[a]	cc-pVQZ[a]	aug-cc-pVQZ[a]	cc-pV∞z[b]	aug-cc-pV∞Z[b]	cc-pcVDZ[c]	cc-pcVTZ[c]
IIn	ΔHF	14.841	13.835	13.329	13.387	13.032	13.291	13.116	*12.826*	***12.750***		
	+MP2	–12.633	–12.412	–12.783	–12.878	–12.647	–12.702	–12.657	*–12.354*	***–12.261***	–0.162	**–0.161**
	+MP3	2.634	2.636	2.155	2.343	2.283	2.399	2.181	*2.068*	***2.042***	0.121	**0.113**
	+CCSD	2.713	2.494	2.281	2.316	2.231	2.246		***2.143***		0.055	**0.074**
	+CCSD(T)	–2.115	–2.011	–1.847	–1.915	**–2.334**					**0.007**	
	total	5.440	4.542	3.135	3.098	2.77	*2.900*[d]	*2.552*[d]	*2.353*[d]	*2.344*[d]	*2.365*	*2.370*[e]
IVn	ΔHF	7.376	6.901	6.807	6.665	6.615	6.594	6.587	*6.623*	***6.532***		
	+MP2	–1.254	–1.354	–1.408	–1.661	–1.681	–1.72	–1.714	*–1.656*	***–1.549***	–0.003	**–0.002**
	+MP3	0.403	0.386	0.405	0.393	0.432	0.439	0.418	*0.402*	***0.255***	0.012	**0.011**
	+CCSD	0.056	0.048	0.045	0.042	0.040	0.038		***0.037***		0.006	**0.003**
	+CCSD(T)	–0.062	–0.056	–0.058	–0.062	**–0.088**					**0.002**	
	total	6.517	5.928	5.792	5.377	5.313	*5.259*[d]	*5.234*[d]	*5.315*[d]	*5.187*[d]	*5.194*	*5.199*[e]
IIIp	ΔHF	8.952	8.556	8.346	8.305	8.201	8.218	8.213	*8.113*	***8.119***		
	+MP2	–2.012	–2.015	–2.053	–2.012	–2.008	–1.993	–1.979	*–1.982*	***–1.989***	–0.003	**–0.002**
	+MP3	0.971	0.849	0.832	0.819	0.784	0.798	0.790	*0.803*	***0.786***	0.104	**0.132**
	+CCSD	0.856	0.705	0.681	0.676	0.653	0.664		***0.632***		0.036	**0.026**
	+CCSD(T)	–0.435	–0.434	–0.404	–0.411	**–0.412**					**–0.002**	
	total	8.332	7.661	7.402	7.377	7.218	*7.275*[d]	*7.276*[d]	*7.154*[d]	*7.160*[d]	*7.295*	*7.316*[e]
Vn	ΔHF	12.218	12.036	11.821	11.632	11.729	11.854	11.861	*11.785*	***11.743***		
	+MP2	–1.624	–1.612	–1.446	–1.295	–1.271	–1.162	–1.145	*–1.187*	***–1.201***	–0.005	**–0.002**
	+MP3	1.156	0.897	0.697	0.702	0.675	0.698	0.702	*0.721*	***0.701***	0.008	**0.006**
	+CCSD	0.431	0.375	0.172	0.158	0.142	0.153		***0.161***		0.004	**0.003**
	+CCSD(T)	–0.021	–0.034	–0.086	–0.091	**–0.051**					**–0.006**	
	total	12.160	11.662	11.158	11.106	11.224	*11.492*[d]	*11.520*[d]	*11.429*[d]	*11.353*[d]	*11.354*	*11.350*[e]
VIp	ΔHF	26.156	24.877	24.705	23.617	23.523	23.442	23.416	*23.978*	***23.515***		
	+MP2	–5.627	–4.802	–4.967	–3.461	–3.394	–3.225	–3.235	*–3.452*	***–3.418***	–0.010	**–0.009**
	+MP3	–0.716	–0.724	–0.502	–0.401	–0.293	–0.302	–0.211	*–0.469*	***–0.199***	–0.002	**–0.003**
	+CCSD	0.485	0.506	0.701	0.857	0.858	0.861		***0.887***		0.007	**0.005**
	+CCSD(T)	26.156	–0.603	–0.601	–0.523	**–0.598**					**0.004**	
	total	19.617	19.254	19.335	20.134	20.096	*20.182*[d]	*20.233*[d]	*20.346*[d]	*20.187*[d]	*20.186*	*20.180*[e]
VIIp	ΔHF	34.745	32.814	32.236	32.322	32.060	31.985	31.831	*31.612*	***31.702***		
	+MP2	–7.297	–7.887	–8.188	–8.551	–8.724	–8.043	–8.134	*–8.864*	***–8.646***	–0.104	**–0.092**
	+MP3	1.347	1.405	1.426	1.537	1.538	1.556	1.797	*1.463*	***1.528***	0.096	**0.089**
	+CCSD	1.676	1.685	1.722	1.645	1.518	1.471		***1.485***		0.032	**0.033**
	+CCSD(T)	–1.580	–1.653	–1.629	–1.795	**–1.885**					**–0.013**	
	total	28.891	26.364	25.567	25.158	24.507	*25.084*[d]	*25.350*[d]	*23.811*[d]	*24.184*[d]	*24.195*	*24.214*[e]
VIIIn	ΔHF	33.994	31.502	31.262	30.652	30.558	30.518	30.443	*30.641*	***30.589***		
	+MP2	–5.798	–5.541	–5.323	–5.284	–5.138	–5.102	–5.169	*–5.178*	***–5.185***	–0.118	**–0.106**
	+MP3	–0.328	–0.305	–0.296	–0.254	–0.032	–0.041	–0.041	*–0.046*	***—-0.051***	0.015	**0.016**
	+CCSD	0.796	0.817	0.856	0.871	0.964	0.951		***0.632***		0.014	**0.010**
	+CCSD(T)	–0.817	–0.832	–0.764	–0.783	**–0.754**					**–0.006**	
	total	27.847	25.641	25.735	25.202	25.598	*25.572*[d]	*25.429*[d]	*25.295*[d]	*25.231*[d]	*25.136*	*25.151*[e]

[a] Frozen core calculations
[b] Extrapolation of HF total energies obtained by using Eq. (1); correlated total energies extrapolated to complete basis set obtained by using Eq. (2).
[c] Core corrections.
[d] Extrapolation made by adding value(s) from the cell to the left.
[e] Best estimate for each conformer (obtained by summing values in bold).

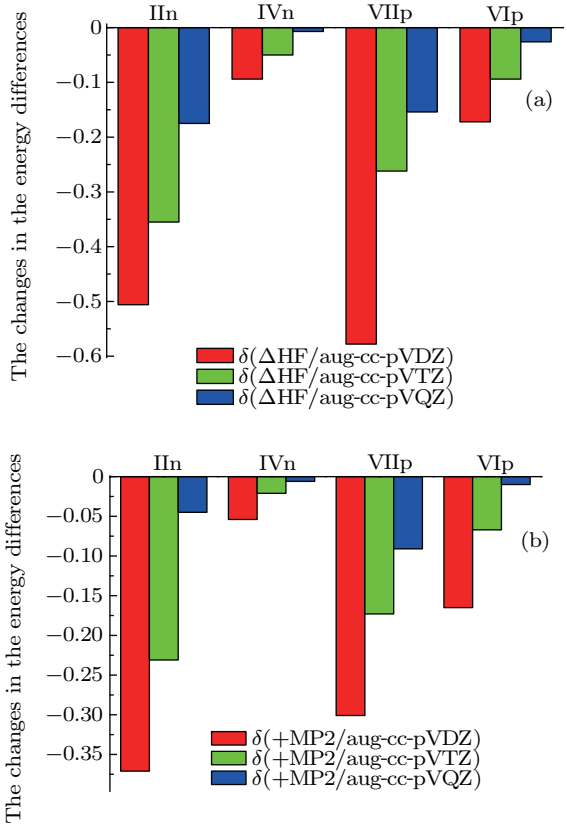


Fig. 2. (color online) Influences of diffusion functions on the change in relative energy for conformers with (IIn and VIIp) and without (IVn and VIp) intramolecular H-bond at HF and MP2 theory levels. δ(ΔHF/aug-cc-pVDZ)= $\Delta E_{\Delta\mathrm{HF/aug-cc-pVDZ}} - \Delta E_{\Delta\mathrm{HF/cc-pVDZ}}$, $\delta(+\mathrm{MP2/aug\text{-}cc\text{-}pVDZ}) = \Delta E_{+\mathrm{MP2/aug-cc-pVDZ}} - \Delta E_{+\mathrm{MP2/cc-pVDZ}}$.

On inspecting Table 2, it is evident that the MP2 corrections to the ΔHF relative energies are the most significant, independent of conformer type. The differences between CCSD/ aug-cc-pVTZ and CCSD/cc-pVQZ predictions (< 0.05 kJ/mol) indicate that the energy correction at the CCSD/aug-cc-pVTZ level has converged. To be more specific, on the one hand, when moving from cc-pVTZ to cc-pVQZ basis sets, the change in the energy difference is rather limited and less than 0.2 kJ/mol. On the other hand, due to the intramolecular through-bond O–H$\cdots$N hydrogen bond in IIn and VIIp conformers of glycine, the obvious effects of diffuse functions on the obtained energy differences at the lower-order theory levels (HF and MP2 levels) are found (see Fig. 2). Energetically close IVn and VIp conformations are chosen for comparison. Figure 2(a) shows that at an HF theory level, after adding diffuse functions into the cc-pVDZ basis, the energy differences of IIn–Ip and VIIp–Ip decrease by 0.506 kJ/mol and 0.578 kJ/mol, respectively, which are larger than the changes in the IVn–Ip and VIp–Ip energy differences, 0.094 kJ/mol and 0.172 kJ/mol. Similarly, compared with MP2/cc-pVDZ predictions, MP2/aug-cc-pVDZ ones for IIn–Ip and VIIp–Ip energy differences further drop by 0.371 kJ/mol, and 0.301 kJ/mol. However, at the same theoretical level, the influences of diffuse functions on the relative energy of IVn and VIp conformers without an intramolecular hydrogen bond are limited (0.054 kJ/mol and 0.165 kJ/mol). In addition, the intramolecular H-bond worsens the convergence of IIn and VIIp conformers. It is clear from Table 2 (see the two rightmost entries) that the influence of frozen core approximation on the relative energy is not very obvious, below 0.02 kJ/mol. From the above discussion, the best values of relative energies including core correction for the IIn, IVn, IIIp, Vn, VIp, VIIp, and VIIIn conformers are 2.370, 5.199, 7.316, 11.350, 20.180, 24.214, and 25.151 kJ/mol, respectively, which are in line with earlier studies.[25]

3.2. Evolution of conformational abundance

In this subsection, the evolutions of conformational abundances for glycine with temperature, in a range of 298 K-500 K, are calculated by using the standard Boltzmann formula $\rho_i \exp(-\Delta G_i/\mathrm{RT})$ with and without taking into account the influence of internal hindered rotation. The values of symmetry number ρ_i in the expression for evaluating n_i of the species i are set to be 4 and 2 for the C_1 and C_s symmetry point groups, respectively. For example, at room temperature, we calculate the relative Gibbs free energy differences at the B3LYP/aug-cc-pVTZ theory level by using the rigid rotor-harmonic oscillator (RRHO) and the hindered rotation approximation. From ΔG_{298} and ρ_i, the corresponding molar fraction for individual structure at a standard temperature is easy to calculate, and conformer abundances are similarly obtained at other temperatures. For inspecting the influences of temperature on the relative mole fraction of glycine conformers, the changes in conformational abundances with temperature are given in Fig. 3. The abundances for each of the conformers at different temperatures obtained by using the RRHO model (or without considering the hindered rotation) are provided in Fig. 3(a). It is clear that (i) the weight of the most stable Ip structure decreases with increasing temperature; (ii) the abundance of IIn conformer keeps almost constant ($\sim 20\%$) in a wide temperature range of (298 K–475 K), and even at the higher temperatures ($T > 475$ K) considered, only a very slight decrease is observed; (iii) however, from the examination of the abundances of the IVn and Vn conformers, a slow monotonic increase with temperature is found. In addition, the weight of the Vn structure remains extremely limited and exceeds 3% only at temperatures above 450 K; (iv) the population of IIIp conformer monotonically and quickly increases and goes to a value of 25% at 500 K, which is larger than the abundances of IIn and IVn rotamers (~ 20 % and 15%) at the same temperature; (v) finally, the weights of the VIp, VIIp, and VIIIn conformers remain totally negligible (order of 10^{-4}) in the whole considered temperature range. Figure 3(b) shows the conformer abundances of glycine derived from the Boltzmann equation for temperature between 298 K and 500 K by taking into account the influence of hindered rotations. The same evolution trends of conformer abundances in all cases are observed. For instance, as the temperature goes up from 298 K to 500 K, the weight of the most stable Ip rotamer decreases,

the abundance of the second stable IIn conformer keeps almost constant, the mole fractions of IVn and IIIp structures increase. For the remaining four species of Vn, VIp, VIIp, and VIIIn, their weights are negligible, no matter whether the RRHO model or rigid-rotor hindered rotation model is used. So these four structures may be "electrostatically forbidden". However, significant quantitative influences of hindered rotation on the calculated abundances of Ip and IIIp rotamers at various temperatures are observed (Fig. 3(b)). To be more specific, when internal hindered rotation is considered, at any temperature, the Ip conformer is the most abundant species. But, figure 3(a) shows that at the level of RRHO, only at temperatures less than 340 K, the weight of Ip conformer will dominate in the conformational mixture. Moreover, the effect of hindered rotation on the weight of IIIp species is particularly strong. Comparing with Fig. 3(a), a slow, not rapid, monotonic increase with temperature is found in Fig. 3(b). At 410 K, hindered rotation model predicts the value of abundance of IIIp is about 5%, which is much less than 19.6% provided by the RRHO model and is more realistic.[15,16]

For comparison purposes, our predicted theoretically conformer abundances, the results obtained by Balabin, Brion, and Nguyen at 410, 438, and 500 K are listed in Table 3. It is found from Table 3 that the conformational weight for glycine, obtained by taking an internal hindered rotation model into account, differs obviously from the computed results based solely on RRHO approximation or internal energy difference. For example, for the four most stable conformers of free glycine, Ip, IIn, IVn, and IIIp, the abundances obtained in this way at 410 K are described by mole fractions of 46%, 11%, 7%, and 35%, whereas the present corrected evaluations show the values of 56%, 23.4%, 13.6%, and 6.5%, respectively. It is worth pointing out that to date, only the Ip, IIn, and IVn three structures have been confirmed to co-exist at 380 K using low-frequency, gas-phase vibrational (Raman) spectroscopy (160 cm^{-1}–450 cm^{-1}),[16] and the fourth band associated with IIIp structure is not observed. Clearly, our calculated data are in agreement with the experimental results, which indicate that the influence of the internal hindered rotation on the relative mole fraction of glycine cannot be ignored. In addition, even though IIIp structure is hard to observe because the weight is too small (6.5%), the fact of an appearance of a IIIp conformation was supported by Balabin.[16] Finally, a comparison of the experimental jet-cooled Raman spectra with Raman spectrum at 380 K indicates a change in the IVn/IIn band intensity ratio.[15,16] The increase of the IVn signal at 380 K is expected because with temperature increasing, the weight of IIn conformer almost remains constant, but the relative abundance of IVn rotamer goes up. In summary, the calculated evolution of conformational abundances with temperature is in agreement with the Raman spectrum:[15,16] (I) at lower temperature, a large amount of Ip and the structure of the second most stable glycine conformer IIn are confirmed, the third band corresponding to IVn conformation is found; (II) at higher temperature, the evidence is presented for the fourth (IIIp) conformation.

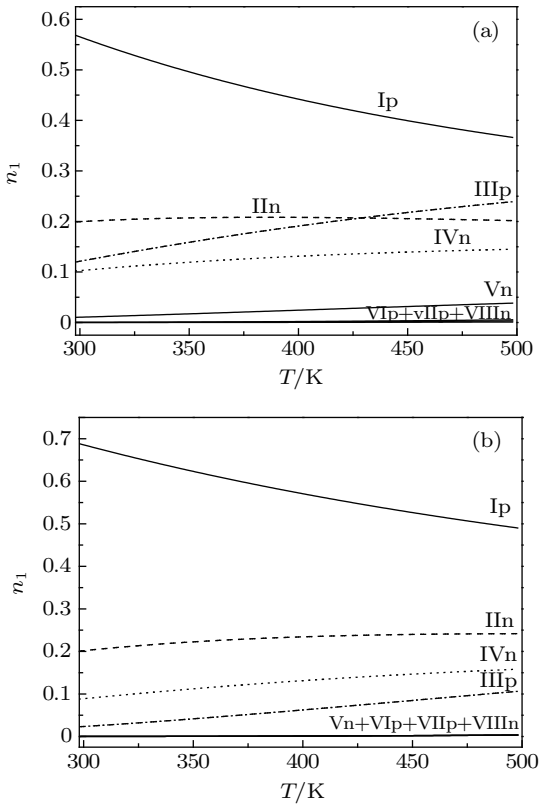


Fig. 3. Evolutions of the glycine conformational abundance with temperature (a) without and (b) with considering hindered rotations.

Table 3. Conformer distribution (%) at selected different temperatures.

	410 K			438 K				500 K			
Ip	43[a]	56[b]	46[c]	41[a]	53[b]	55[d]	53[e]	37[a]	49[b]	56[f]	45[g]
IIn	21	23	11	21	24	20	9	21	24	21	8
IVn	13	13	7	14	14.7	13	7	14	16	0	35
IIIp	**20**	**6**	**35**	**21**	**8**	**9**	**30**	**24**	**11**	**16**	**8**
Vn	3.0	0.0	1	3	0.3	3	2	4	0	7	5
VIp	0.0	0.0	0	0	0	0.3	0.3	0	0	0	0
VIIp	0.0	0.0	0	0	0	0.1	0.1	0	0	0	0
VIIIn	0.0	0.0	0	0	0	0.1	0.4	0	0	0	0

[a]Our predictions for each of the conformers of interest without considering hindered rotations.
[b]Our predictions for each of the conformers of interest with considering hindered rotations.
[c]See Ref. [16]; [d]See Ref. [11]; [e]See Ref. [12]; [f]See Ref. [26]; [g]See Ref. [37].

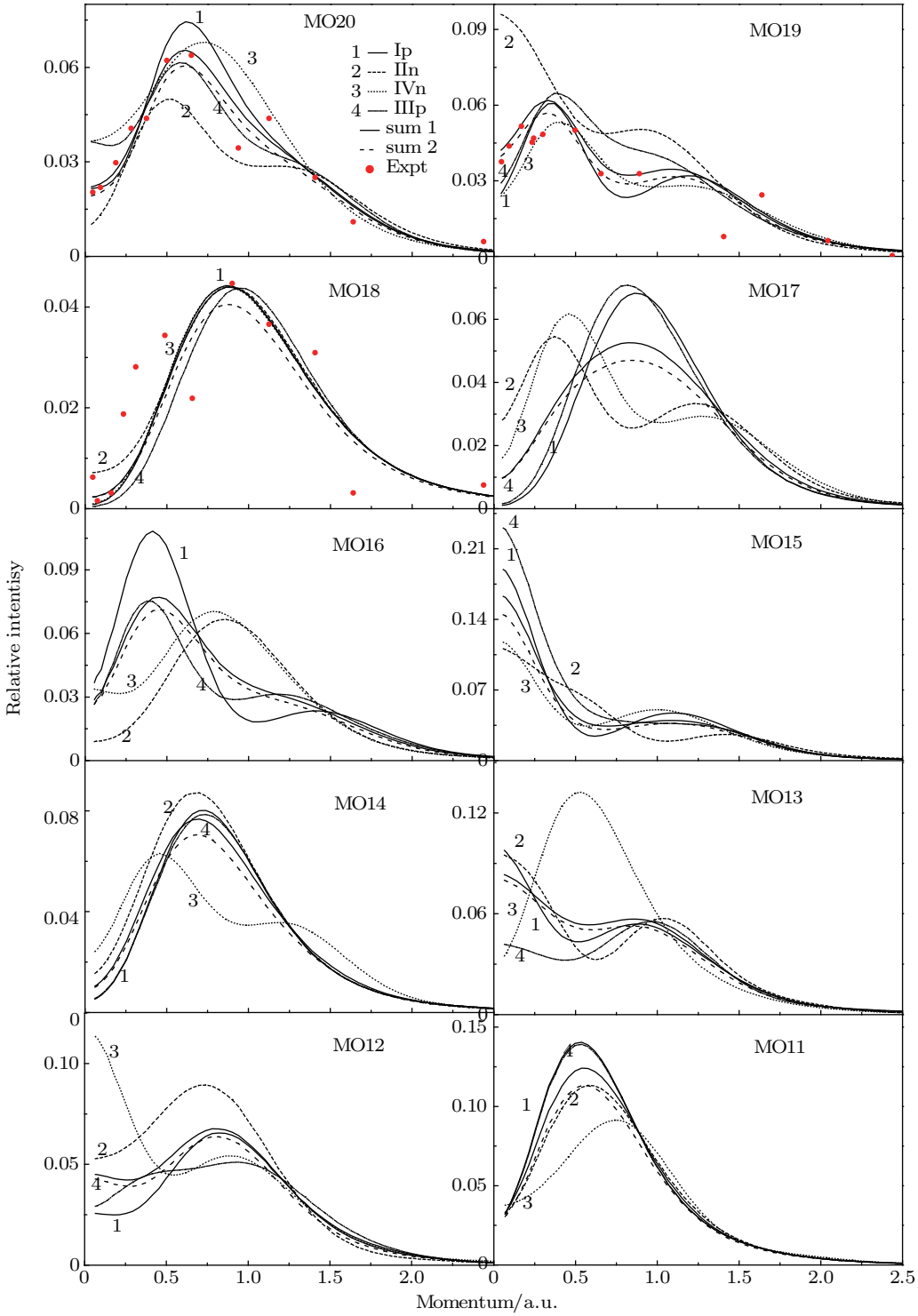


Fig. 4. (color online) Convolved and spherically averaged momentum distributions of glycine. Boltzmann weighted contributions of Ip (53%), IIn (24%), IVn (14.7%), and IIIp (8%) conformer are given. Theoretical sum1 is the scaled sum of the individual distribution for four structures (Ip, IIn, IVn, and IIIp) according to relative Boltzmann populations at 438 K and IIIp conformer is not included in sum 2. Solid dots are the EMS experimental data, cited from Ref. [12].

Electron momentum spectroscopy (EMS)[38–43] is an effective experimental technique for investigating the conformational change, because the imaged electron momentum density distributions of individual atomic and molecular orbitals are very sensitive to the relative population change among the conformers. For the sake of completeness, the theoretical spherically averaged (e, 2e) electron momentum distributions with taking into account the individual contributions from Ip, IIn, IVn and IIIp conformers are compared with the experimental momentum files of free glycine at an experimental temperature of 438 K,[12] since the thermodynamic calculations at the hindered rotation level indicate that the total weight of the remaining four conformers (Vn, VIp, VIIp, and VIIIn) is about 0.3% (see Table 3). From Fig. 4, the good quantitative agree-

ment between the theoretical result and experimental data for molecular orbital 20 is obtained. However, in the low momentum region (0.25 a.u.–0.70 a.u.) of molecular orbitals 19 and 18, the calculations overestimate the experimental intensity in the one case and underestimate in the other case. Brion *et al*.[12] mentioned that this disagreement is mainly due to "the limitations in the energy resolution (1.5 eV) and the uncertainties in the deconvolution procedure used to obtain experimental momentum profiles for these energetically closely spaced orbitals". Besides, the discrepancy between the sum 1 (Ip, IIn, IVn, and IIIp) and sum 2 (Ip, IIn, and IVn) supports the idea of an appearance of IIIp conformation. Further EMS experimental measurements with a higher resolution on glycine at various temperatures are needed to improve our understanding of the influence of conformational abundances on the (e, 2e) experimental orbital momentum distribution.

3.3. Interconversion of conformers

In order to provide a correct explanation for the published experimental observations, the conformational interconversion of glycine is discussed in this section. The calculations indicate that the influence of temperature on either of barrier height and rate constant is obvious, so only the rotational bond, barrier height (kJ/mol), and rate constant (s^{-1}) of conformational interconversion for glycine at 438 K are shown in Table 4. The thermal energy contained in glycine molecules at 438 K is predicted to be no more than 26 kJ/mol. See Table 4, compared with the thermal energy, the barrier heights for conformational interconversions 7 (65.21/50.79 kJ/mol) and 8 (73.84/42.31 kJ/mol) are too high to be feasible, which is a correct explanation for constant population fractions of IIn and VIIp isomers in the considered temperature range (see Fig. 3). For interconversion 6, because the thermal energy of $\sim$ 26 kJ/mol in IVn structrue is less than the barrier (46.52 kJ/mole) separating conformer IVn from conformer VIIn, the interconversion from IVn to VIIIn does not occur. Even though VIIIn has enough energy to pass over the barrier height for relaxation from higher energy VIIIn to lower energy IVn, say, 21.32 kJ/mol, the mole fraction of this conformer is too small ($\sim 0.04\%$). As a result, the weight of the VIIIn conformer does not change obviously in a temperature range from 298 K to 500 K. Interconversion 5 is similar to 6. So, the abundance of VIp is "frozen" and independent of temperature. The barriers to conformational interconversions 1, 2, 3, and 4 are low enough to expect relaxation/formation of isomers at 438 K. In detail, the rate constants of interconversion from Ip to higher energy IVn and IIIp are a hundredfold greater than the corresponding ones of relaxation ($k_{\mathrm{Ip}\rightarrow\mathrm{IVn}} > k_{\mathrm{Ip}\leftarrow\mathrm{IVn}}$ and $k_{\mathrm{Ip}\rightarrow\mathrm{IIIp}} > k_{\mathrm{Ip}\leftarrow\mathrm{IIIp}}$), which leads to the decrease in the weight of Ip with temperature rising. Therefore, the proportions of IVp and IIIp will be augmented from the interconversion of Ip. In addition, the fact that $k_{\mathrm{IIIp}\leftarrow\mathrm{Vn}}$ is greater than $k_{\mathrm{IVn}\rightarrow\mathrm{Vn}}$ can explain that Vn isomer is not detected in experimental spectrum studies of glycine.[12,16] As the temperature drops, IVn and IIIp isomers can relax to the most stable Ip structure and the proportion of Ip will be augmented.

Table 4. Rotational bond, barrier height (kJ/mol), and interconversion rate constant (s^{-1}) of conformational interconversion for glycine at 438 K.

Interconversion		Rotational bond	Barrier height		Interconversion constant	
			L→H[a]	H→L[b]	L→H[c]	H→L[d]
1	Ip↔IVn	C–N	11.25	4.21	3.2×10^{12}	1.4×10^{10}
2	IIIp↔Vn	C–N	15.12	8.36	2.5×10^{10}	1.6×10^{11}
3	Ip↔IIIp	C–C	12.83	3.85	7.5×10^{11}	1.3×10^{9}
4	IVn↔Vn	C–C	19.46	9.87	6.8×10^{9}	3.5×10^{8}
5	Ip↔VIp	C-O	49.36	20.45	3.5×10^{6}	4.8×10^{7}
6	IVn↔VIIIn	C–O	46.52	21.32	1.4×10^{7}	7.7×10^{7}
7	IIn↔Vn	C–O	65.21	50.79	2.8×10^{5}	2.7×10^{6}
8	IIn↔VIIp	C–N	73.84	42.31	3.1×10^{5}	4.5×10^{6}

[a]Barrier height (kJ/mol) for the formation from the lower energy form of glycine to the higher energy one.
[b]Barrier height (kJ/mol) for relaxation from the higher energy form of glycine to the lower energy one.
[c]Interconversoion rate constant (s^{-1}) of formation from the lower energy form of glycine to the higher energy one.
[d]Interconversion rate constant (s^{-1}) of relaxation from the higher energy form of glycine to the lower energy one.

4. Conclusions

The conformational equilibrium, the conformational abundance evolution over a range of 298 K–500 K, and the conformational interconversion of glycine in the gas phase have been investigated thoroughly. The specific process and findings are as follows.

i) The relative energies of eight glycine conformers are determined by means of focal point analysis. The accuracy of a few tenths of kJ/mol is reached. The best values of relative energies obtained from *ab initio* methods for the IIn, IVn, IIIp, Vn, VIp, VIIp, and VIIIn conformers are 2.370, 5.199, 7.316, 11.350, 20.180, 24.214, and 25.151 kJ/mol, respectively,

ii) Based on the relative energies and Boltzmann statis-

tical thermostatistical analysis with and without considering hindered rotation, the conformer abundances at different temperatures are calculated for glycine. Compared with the experimental studies, the values of abundances of various structures predicted using the hindered rotation model are more realistic, particularly for the IIIp conformer.

iii) None of conformational interconversions 7 (IIn↔Vn), 8 (IIn↔VIIp), Ip→VIp, and IVn→ VIIIn can occur because this would require surmounting large barriers. In addition, due to the very small initial mole fractions of VIp and VIIIn, neither of the relaxations of VIp to Ip and VIIIn to IVn almost affect the weight of Ip or the weight of IVn.

iv) Since the rate constants of interconversion from Ip to higher energy IVn and IIIp are greater than the ones of relaxations of IVn and IIIp to Ip ($k_{\mathrm{Ip}\rightarrow\mathrm{IVn}} > k_{\mathrm{Ip}\leftarrow\mathrm{IVn}}$ and $k_{\mathrm{Ip}\rightarrow\mathrm{IIIp}} > k_{\mathrm{Ip}\leftarrow\mathrm{IIIp}}$), the proportion of Ip will decrease and the proportions of IVp and IIIp will be augmented with temperature rising.

v) Due to the fact that $k_{\mathrm{IIIp}\leftarrow\mathrm{Vn}}$ is greater than $k_{\mathrm{IVn}\rightarrow\mathrm{Vn}}$, Vn isomer cannot be detected in experimental spectrum studies of glycine.

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