Conformational Distribution of Gas-phase Glycerol

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Combining ab initio and statistical mechanics calculations we have determined the conformational distribution of gas-phase glycerol at different temperatures. The obtained results are consistent with infrared spectroscopy and electron diffraction measurements and are in excellent agreement with previous molecular dynamics simulation data.

In a recent paper[1] we have calculated the infrared absorption of various conformers of glycerol using density functional theory. These conformers are shown in Figure 1. The ab initio data were used in a fitting procedure of the experimental infrared spectrum of gas-phase glycerol.[2] The results indicated that, at 498 K, glycerol is present as a mixture of two conformers, namely αα and αγ. Unfortunately the fit was not able to give quantitative results because of the large computational error (see discussion in ref 1). However, our conclusions were qualitatively similar to those obtained with electron diffraction measurements[3] and with molecular dynamics simulations[4] using empirical potential models.

At variance with these conclusions, the best fit to the supersonic jet rotational spectrum of a gas sample at 423 K was obtained assuming a distribution of $\gamma\gamma$ and αγ conformers.[5] Although the independent experimental measurements of the vibrational infrared and rotational microwave spectra refer to comparable thermodynamic conditions, they give contradictory indications on the conformational distribution that cannot be explained on the basis of the temperature difference. In view of this discrepancy, we thought it useful to search for an additional independent evidence for the conformational composition of gas-phase glycerol.

In this paper we report on a quantitatively reliable estimate of the conformational distribution of glycerol in gas phase, by computing the molecular partition function and the equilibrium constants using the results of accurate ab initio data.

In gas-phase glycerol, for any pair of conformational species I and J, the following conformational equilibrium holds

$$I \rightleftharpoons J \tag{1}$$

In the hypothesis of an ideal mixture, the equilibrium constant K_{IJ} can be determined from the knowledge of the molecular partition functions[6]

$$\frac{N_J}{N_I} = \frac{d_J q_J}{d_I q_I} = K_{IJ} \tag{2}$$

where N_J and N_I are the molar concentrations. The d_I and d_J factors correspond to the structural degeneracy of the conformers, namely to the number of different conformational enantiomers. For all of the considered conformers (see Figure 1) $d = 2$, except for αα3 ($d = 1$) because of the presence of a symmetry plane. In the Born−Oppenheimer approximation and neglecting vibro-rotational coupling, the molecular partition function can be factorized into its translational, rotational, vibrational, electronic, and nuclear parts, i.e., $q = q_{\mathrm{trans}}\, q_{\mathrm{rot}}\, q_{\mathrm{vib}}\, q_{\mathrm{elec}}\, q_{\mathrm{nucl}}$. The translational and nuclear partition functions are identical for all of the species and therefore they are irrelevant for the equilibrium constant of eq 2. The rotational partition function for an asymmetric top such as any glycerol conformer I is given by[6]

$$q_{\mathrm{rot}}^{(I)} = \pi^{1/2} \left(\frac{8\pi^2}{\beta h^2}\right)^{3/2} (I_A^{(I)}\, I_B^{(I)}\, I_C^{(I)})^{1/2} \tag{3}$$

where $I_A^{(I)}$, $I_B^{(I)}$, and $I_C^{(I)}$ are the principal moments of inertia, h is the Planck constant and $\beta = 1/(k_B T)$. The vibrational partition function is given by

$$q_{\mathrm{vib}}^{(I)} = \prod_j \frac{\exp(-\beta h \nu_j^{(I)}/2)}{1 - \exp(-\beta h \nu_j^{(I)})} \tag{4}$$

where j goes over the 36 vibrational frequencies $\nu_j^{(I)}$. Finally the electronic partition function is given by

$$q_{\mathrm{elec}}^{(I)} = \exp(-\beta E_g^{(I)}) \tag{5}$$

where $E_g^{(I)}$ is the (non degenerate) ground-state electronic energy of the Ith conformer. Using the factorization property of the molecular partition function, the equilibrium constant K_{IJ} (eq 2) can be written as

$$K_{IJ} = K_{\mathrm{rot}} K_{\mathrm{vib}} K_{\mathrm{elec}} = \frac{q_{\mathrm{rot}}^{(J)}}{q_{\mathrm{rot}}^{(I)}} \frac{q_{\mathrm{vib}}^{(J)}}{q_{\mathrm{vib}}^{(I)}} \frac{q_{\mathrm{elec}}^{(J)}}{q_{\mathrm{elec}}^{(I)}} \tag{6}$$

Using the ab initio data relative to the various conformers (all the ab initio data were obtained by the Gaussian98 package[7]), i.e., inertia moments, vibrational frequencies, and ground-state electronic energies, the gas-phase partition functions (eqs 3−5) can be calculated. From these, via eq 6, the

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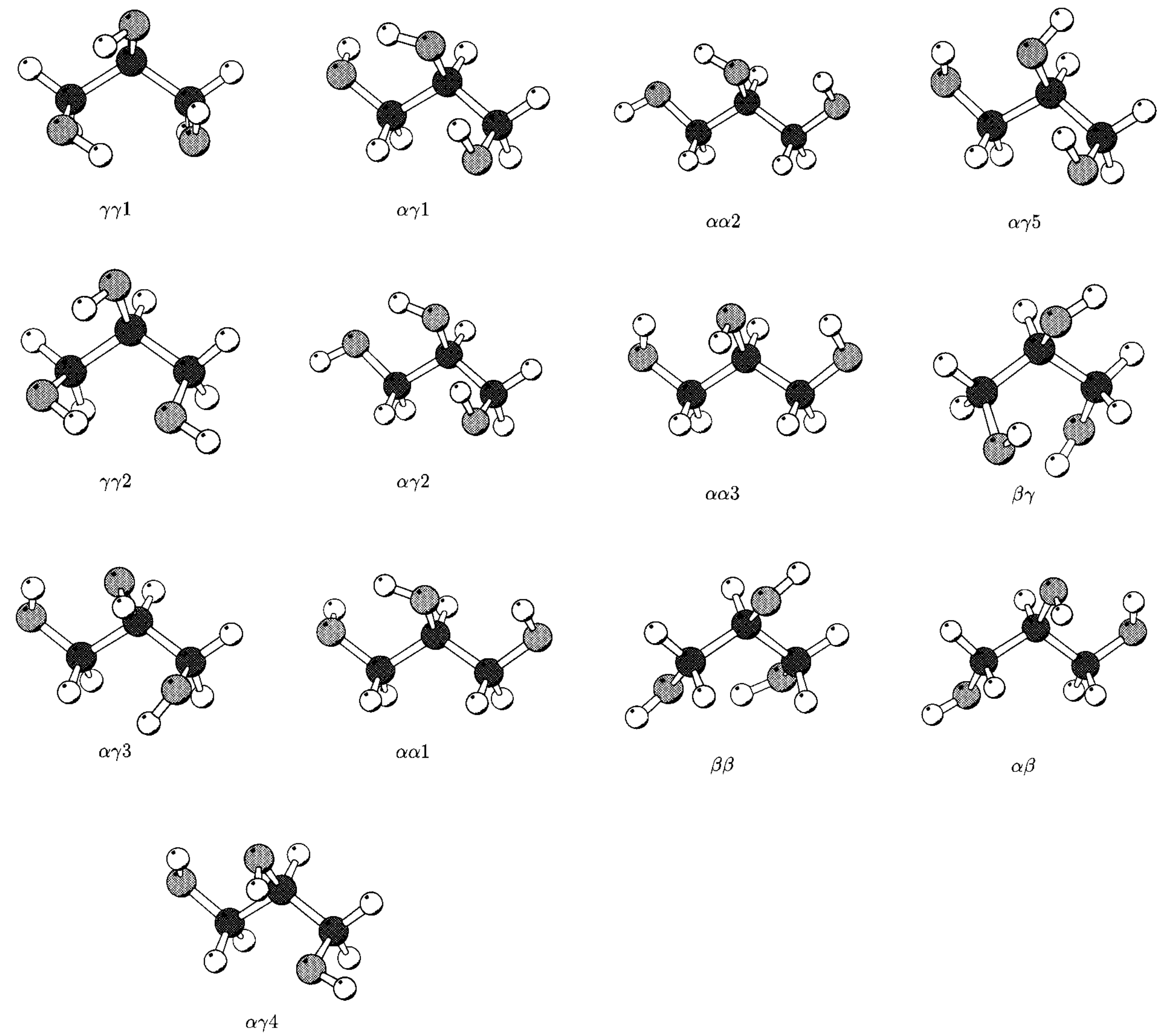
$\gamma\gamma1$ $\alpha\gamma1$ $\alpha\alpha2$ $\alpha\gamma5$

$\gamma\gamma2$ $\alpha\gamma2$ $\alpha\alpha3$ $\beta\gamma$

$\alpha\gamma3$ $\alpha\alpha1$ $\beta\beta$ $\alpha\beta$

$\alpha\gamma4$

Figure 1. Structures of the glycerol conformers.

chemical equilibrium constants between the various species, and hence the conformational distribution, are determined.

At the B3-LYP/6-31G(d) level of theory,[8-10] inertia moments and vibrational frequencies within few percent from the experimental counterparts are generally obtained.[11-16] The size of the basis set, however, is not sufficient to obtain reliable ground state *relative* electronic energies.[17] To minimize the error on the ab initio energies, it has been suggested[17] to optimize the structure at the B3-LYP/6-31G(d) level and then to compute the ground-state electronic energy using a single-point calculation with a much larger basis set, such as 6-311+G(3df,2p). Using this procedure, the average errors on molecular properties, such as atomization energies or first ionization potentials, were found to be[17] comparable to or even smaller than those obtained with very expensive correlated methods such as MP2[18] with a large basis set.

The electronic energies of the conformers of Figure 1 computed with B3-LYP using the small 6-31G(d) and the large 6-311+G(3df,2p) basis sets are reported in Table 1. All structures were optimized with the small basis set. As already found in ours[1] and in other ab initio calculations,[19] $\gamma\gamma1$ turns out to be the most stable conformer. However, as it can be seen from the table, the 6-31G(d) basis set gives larger energy gaps between the $\gamma\gamma1$ and other conformers with respect to the 6-311+G(3df,2p) basis set. For instance, the energy difference $\gamma\gamma1$-$\alpha\alpha2$ reduces from 14.7 to 2.1 kJ mol^{-1} going from the 6-31G(d) to the 6-311+G(3df,2p) basis set. In Table 2 we report the ratios at 498 K between the various molecular partition functions (vibrational, rotational, and electronic) of the most stable $\gamma\gamma1$ conformer and those corresponding to the other conformers (the vibrational and rotational partition functions have been computed using the data obtained with the small basis set; the computed vibrational frequencies have been rescaled

TABLE 1: Electronic Energies (in kJ mol^{-1}) of the Glycerol Conformers Calculated at the B3-LYP/6-31G(d) and B3-LYP/6-311+G(3df,2p) Level of Theory[a]

	6-311+G(3df,2p)	6-31G(d)
$\alpha\alpha1$	3.13	13.59
$\alpha\alpha2$	2.10	14.73
$\alpha\alpha3$	7.54	17.14
$\alpha\gamma1$	1.87	8.30
$\alpha\gamma2$	0.46	9.32
$\alpha\gamma3$	5.67	12.85
$\alpha\gamma4$	4.10	13.65
$\alpha\gamma5$	5.77	14.92
$\gamma\gamma2$	2.59	8.91
$\alpha\beta$	13.22	26.30
$\beta\beta$	11.74	23.03
$\beta\gamma$	11.19	20.40

[a] $\gamma\gamma1$ conformer is taken as reference for the energy values of all the other conformers.

TABLE 2: Electronic ($K_{\mathrm{elec}} = q_{\mathrm{elec}}^{(\gamma\gamma1)}/q_{\mathrm{elec}}^{(I)}$), Vibrational ($K_{\mathrm{vib}} = q_{\mathrm{vib}}^{(\gamma\gamma1)}/q_{\mathrm{vib}}^{(I)}$) and Rotational ($K_{\mathrm{rot}} = q_{\mathrm{rot}}^{(\gamma\gamma1)}/q_{\mathrm{rot}}^{(I)}$) Contributions to the Constant $K_{I\gamma\gamma1} = K_{\mathrm{elec}}K_{\mathrm{vib}}K_{\mathrm{rot}}$ of the Conformational Equilibrium $I \rightleftharpoons \gamma\gamma1$ at 498 K

I	K_{elec}	K_{vib}	K_{rot}	$K_{I\gamma\gamma1}$
αα1	2.13	0.19	0.88	0.35
αα2	1.66	0.13	0.89	0.19
αα3	6.18	0.23	0.86	1.22
αγ1	1.57	0.38	0.90	0.54
αγ2	1.12	0.27	0.90	0.27
αγ3	3.94	0.34	0.89	1.19
αγ4	2.69	0.22	0.89	0.54
αγ5	4.03	0.22	0.88	0.76
γγ2	1.87	0.38	0.98	0.69
αβ	24.37	0.11	0.80	2.13
ββ	17.05	0.15	0.84	2.13
βγ	14.93	0.09	0.89	1.17

TABLE 3: Conformational Distributions (%) of Glycerol Conformers at Various Temperatures[a]

	298 K	423 K	498 K
γγ1	5.79	4.93	4.50
γγ2	6.30	6.59	6.52
αα1	12.30	12.82	12.75
αα2	27.29	24.53	23.22
αα3	0.89	1.55	1.84
αγ1	9.25	8.78	8.40
αγ2	23.56	18.56	16.67
αγ3	2.29	3.37	3.78
αγ4	6.69	8.02	8.38
αγ5	3.69	5.27	5.88
αβ	0.44	1.41	2.11
ββ	0.52	1.48	2.11
βγ	0.94	2.69	3.85
αα	40.49	38.90	37.81
αγ	45.50	44.01	43.10
γγ	12.09	11.52	11.02

[a] γγ, αγ and αα are the total concentrations obtained by summing up the contributions of the identical backbone conformers.

by the factor 0.928 as proposed by Rauhut and Pulay[13]). The product of these ratios ($K_{I\gamma\gamma1}$ in Table 2) yields the concentration of the γγ1 conformer relative to that of the *I*th conformer. According to ab initio calculations, γγ1 is the most stable conformer, hence its presence in the gas phase should be favored with respect to all of the other conformers. However γγ1 has a very "rigid" and "compact" structure with correspondingly small vibrational and rotational partition functions compared to more open and less rigid forms such as αα or αγ. This behavior is confirmed by K_{elec}, K_{rot}, and K_{vib} (see Table 2) which are systematically greater than one (K_{elec}) and less than one (K_{rot} and K_{vib}). The overall balance is in favor of the αα and αγ forms (see relative $K_{I\gamma\gamma1}$ values in Table 2). The conformational distributions at the temperatures of the infrared[1,2] (498 K) and microwave[5] (423 K) experiments, and at room temperature, are shown in Table 3. The αα and αγ backbone conformers have similar concentrations (40−45%) with contributions mainly due to αα1, αα2, and αγ2. The remaining αα and αγ conformers have too high electronic energy (see Table 1) for contributing significantly to the conformational distribution. The γγ backbone conformer has a concentration of about 11−12% with contributions from both γγ1 and γγ2. The αβ, ββ and βγ have concentrations of few units of percentage because of their large electronic energy (see Table 1).

The present results add further support to the conclusions of our previous studies of the infrared spectra[1] and those of the electron diffraction experiments.[3] It can also be remarked that the overall concentrations, as well as their small temperature dependence, are in excellent agreement with those reported in a previous molecular dynamics simulation of the gas-phase glycerol.[4] The results of the present work are still at variance with those of Maccaferri et al.,[5] confirming, as suggested in ref 1, that the supersonic jet expansion in their experiment did not produce an equilibrium distribution.

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