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## Secondary relaxation dynamics in rigid glass-forming molecular liquids with related structures

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The dielectric relaxation in three glass-forming molecular liquids, 1-methylindole (1MID), 5H-5-Methyl-6,7-dihydrocyclopentapyrazine (MDCP), and Quinaldine (QN) is studied focusing on the secondary relaxation and its relation to the structural  $\alpha$ -relaxation. All three glass-formers are rigid and more or less planar molecules with related chemical structures but have dipoles of different strengths at different locations. A strong and fast secondary relaxation is detected in the dielectric spectra of 1MID, while no resolved  $\beta$ -relaxation is observed in MDCP and QN. If the observed secondary relaxation in 1MID is identified with the Johari-Goldstein (JG)  $\beta$ -relaxation, then apparently the relation between the  $\alpha$ - and  $\beta$ -relaxation frequencies of 1MID is not in accord with the Coupling Model (CM). The possibility of the violation of the prediction in 1MID as due to either the formation of hydrogen-bond induced clusters or the involvement of intramolecular degree of freedom is ruled out. The violation is explained by the secondary relaxation originating from the in-plane rotation of the dipole located on the plane of the rigid molecule, contributing to dielectric loss at higher frequencies and more intense than the JG  $\beta$ -relaxation generated by the out-of-plane rotation. MDCP has smaller dipole moment located in the plane of the molecule; however, presence of the change of curvature of dielectric loss,  $\epsilon''(f)$ , at some frequency on the high-frequency flank of the  $\alpha$ -relaxation reveals the JG  $\beta$ -relaxation in MDCP and which is in accord with the CM prediction. QN has as large an in-plane dipole moment as 1MID, and the absence of the resolved secondary relaxation is explained by the smaller coupling parameter than the latter in the framework of the CM. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4930262>]

### I. INTRODUCTION

Relaxation dynamics of supercooled liquids and glasses have been long-standing problem in basic research and are important for understanding their macroscopic properties.<sup>1-3</sup> Broadband dielectric measurements have become an important method to study the relaxation of molecular liquids and polymers by virtue of the wide temperature and frequency ranges available in experimental investigations.<sup>4</sup> Apart from the structural  $\alpha$ -relaxation which receives by far the most attention in supercooled liquid regime and is generally understood to involve cooperative and dynamically heterogeneous motions,<sup>5</sup> dielectric studies over wide frequency range often detect one or more faster secondary relaxation particularly in the glassy states.<sup>6-8</sup> Not all secondary relaxations found are important for consideration in the problem of glass transition. Among the variety of secondary relaxations are those which show inseparable connection in properties to the  $\alpha$ -relaxation<sup>9-16</sup> and hence are fundamentally important. To distinguish these important secondary relaxations from others, they are called the Johari-Goldstein (JG)  $\beta$ -relaxations<sup>13</sup> for reasons explained in Refs. 7 and 10. Whether the molecules are flexible or rigid, the JG  $\beta$ -relaxation involves the motion of

the entire molecule, and usually it is the slowest secondary relaxation if more than one is present.<sup>10,17-19</sup> Motion of totally rigid molecules such as chlorobenzene,<sup>13</sup> 2-picoline,<sup>15</sup> toluene,<sup>20</sup> and quinaldine (QN)<sup>21</sup> necessarily involves the entire molecule, and hence the unique secondary relaxation showing up in isothermal or isochronal spectra either in the pure state or in mixtures is the JG  $\beta$ -relaxation. Increasing experimental evidences suggest that the JG  $\beta$ -relaxation is universal and fundamentally important dynamical process due to its connection to the structural  $\alpha$ -relaxation<sup>1,22,23</sup> and macroscopic properties in the glassy state.<sup>24,25</sup> For some liquids with narrow frequency dispersion of the  $\alpha$ -relaxation, or equivalently with large value of the exponent,  $\beta_{KWW}$ , in the fractional exponent of the time correlation function in the Kohlrausch-William-Watts (KWW) form,

$$\phi(t) = \exp[-(t/\tau_\alpha)^{\beta_{KWW}}], \quad (1)$$

the JG  $\beta$ -relaxation is not well separated from the dominant  $\alpha$ -relaxation, and it appears as an excess wing on the high frequency flank of the  $\alpha$ -relaxation.<sup>26-28</sup> The Fourier transform of Eq. (1) fits the frequency dispersion of the  $\alpha$ -relaxation.<sup>29</sup>

The understandings of the JG  $\beta$ -relaxations in molecular liquids have been greatly advanced,<sup>7</sup> and the JG  $\beta$ -relaxations are found to be universally present in various glass-formers

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before the onset of the  $\alpha$ -relaxation, whether it is resolved or not, in various glassy materials, preceding the  $\alpha$ -relaxations. Studies found JG  $\beta$ -relaxation bears strong connection to the  $\alpha$ -relaxation. For instance, the  $\alpha$ -relaxation time,  $\tau_\alpha$ , and the JG  $\beta$ -relaxation times,  $\tau_\beta$ , are found to follow basically a relation predicted by the Coupling Model (CM).<sup>6,7,9-15,21,30-32</sup> Experimental studies of flexible molecular glass-formers have found that larger coupling parameter  $n$  gives rise to larger separation between the  $\alpha$ - and  $\beta$ -relaxations in accord with the CM prediction.<sup>7,9-11,33-35</sup> In contrast, the JG  $\beta$ -relaxations have been observed only in a few molecular liquids with rigid structures in the pure state and not in mixtures. The few examples include toluene,<sup>36</sup> isopropylbenzene,<sup>13</sup> and *o*-terphenyl,<sup>13</sup> all have low polarity and the dynamics are governed by the intermolecular potentials of van der Waals. Thus, the relation between the JG  $\beta$ -relaxation and the  $\alpha$ -relaxation, and its dependence on molecular structure needs further investigation for the class of rigid molecular glass-formers. More varieties in the properties of the JG  $\beta$ -relaxations possibly found in polar and rigid molecular liquids would potentially deepen the understanding of the dynamics of glass-forming liquids.

The objective of this paper is to explore the relation between molecular structure and the JG  $\beta$ -relaxations in rigid molecular glass-formers by considering several such substances with difference in structure, polarity, glass forming ability, and intermolecular force. The rigidity of the aromatic rings in all the rigid molecular glass-formers we consider guarantees absence of secondary relaxation involving intramolecular degree of freedom, and the nitrogen is incorporated into the structure to enhance the dielectric strength of all processes appearing in the dielectric spectra. Complexity due to hydrogen bonding is avoided by using the methyl group to replace the H atom in the groups that potentially form H-bonds. Finally, the rigid glass-formers with the higher glass forming ability are chosen, in order to facilitate measurements in the deeply supercooled liquids near the glass transition temperature  $T_g$ . Consequently, three rigid glass-formers with similar structures, 1-methylindole (1MID), 5H-5-Methyl-6,7-dihydrocyclopentapyrazine (MDCP), and QN, are selected to probe the JG  $\beta$ -relaxations in the supercooled liquid regime and the glassy state. Comparison of the dynamics observed in these three glass-formers, as well as in other rigid glass-formers including 2-picoline and toluene, are made to highlight and explain the novel dynamic properties found by this study.

## II. EXPERIMENTAL

1-methylindole (1MID, Sigma-Aldrich  $\geq 97\%$ ) and 5H-5-methyl-6,7-dihydrocyclopentapyrazine (MDCP, Sigma-Aldrich  $\geq 97\%$ ) are used without further purification. The molecular structures are relatively rigid for the three glass-formers, as showed in Fig. 1. The dipole moment is large for 1-methylindole (2.26 D) and for quinaldine (1.86 D),<sup>37</sup> whereas for MDCP, it is quite small, since the two heteroatoms of the aromatic ring contribute opposite dipole moments. The dielectric measurements are carried out using a Novocontrol broadband dielectric spectrometer (Concept 80) equipped by

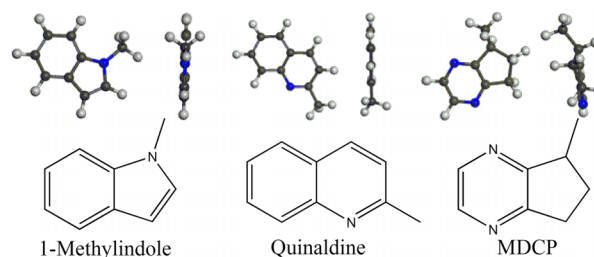


FIG. 1. Chemical structures of 1-methylindole, MDCP, and quinaldine.

a liquid nitrogen cooling system. The dielectric relaxations are isothermally measured at each temperature by holding liquids between two separated brass electrodes by Teflon strips of thickness 25  $\mu\text{m}$ . The scanning frequency range spans from 0.01 Hz to 10 MHz. The temperature is controlled by a Novocontrol Quatro controller with temperature accuracy within 0.1 K. Our dielectric data of QN compare well with that measured previously by Capaccioli and co-workers.<sup>28</sup> Fourier transform infrared (FTIR) spectrum of 1MID is recorded using a KBr disk on an E55+FRA106 type IR spectrometer with spectral range between 500 and 4000  $\text{cm}^{-1}$ .

In the cases such as MDCP and QN where the JG  $\beta$ -relaxation is not resolved, the dielectric data are analyzed using the Havriliak-Negami (HN) equation for the  $\alpha$ -relaxation together with a conductivity term,

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega\tau)^\alpha]^\gamma} + \frac{\sigma_{dc}}{i\epsilon_0\omega}, \quad (2)$$

where  $\epsilon_\infty$  is the high-frequency dielectric constant,  $\Delta\epsilon$  the dielectric strength,  $\tau$  the dielectric relaxation time,  $\alpha$  and  $\gamma$  the profile shape factors of the dispersion, and  $\sigma_{dc}$  is the dc conductivity. In the case where the JG  $\beta$ -relaxation is resolved, an additional HN term to represent it has been used. The  $\alpha$ -relaxation in the dielectric spectra is also analyzed by the Fourier transform of the KWW time correlation function (Eq. (1)) where  $\tau_\alpha$  and the non-exponential or coupling parameter,  $n \equiv (1 - \beta_{KWW})$ , are determined from the fit.

## III. RESULTS AND DISCUSSIONS

The molecular structures of the three glass-formers are presented in Fig. 1, showing that they have some similar basic properties including rigidity of structure, molecular weight, the number of nitrogen atoms, and one methyl group in the rings. The phenyl ring structure and the number of nitrogen atom in 1MID and QN are the same. 1MID and MDCP have a five-atom ring, while QN has the six-atom ring. 1MID distinguishes itself in having the methyl group bonded to the nitrogen atom, while all others have it bonded to the carbon atom.

The isothermal dielectric loss spectra are shown in Figs. 2(a), 2(c), and 2(d) for 1MID, MDCP, and QN in the glassy state and supercooled liquid regime. The red full lines in Figs. 2(a), 2(c), and 2(d) are the fits by the HN function. The fits to the data give the values of  $\Delta\epsilon$ ,  $\tau$ , and the shape parameters  $\alpha$  and  $\gamma$ , which are, respectively, 5,  $-0.6$ , 0.92, and 0.44 for 1MID at 187 K; 1.5,  $-0.85$ , 0.87, and 0.5 for MDCP at 178 K,

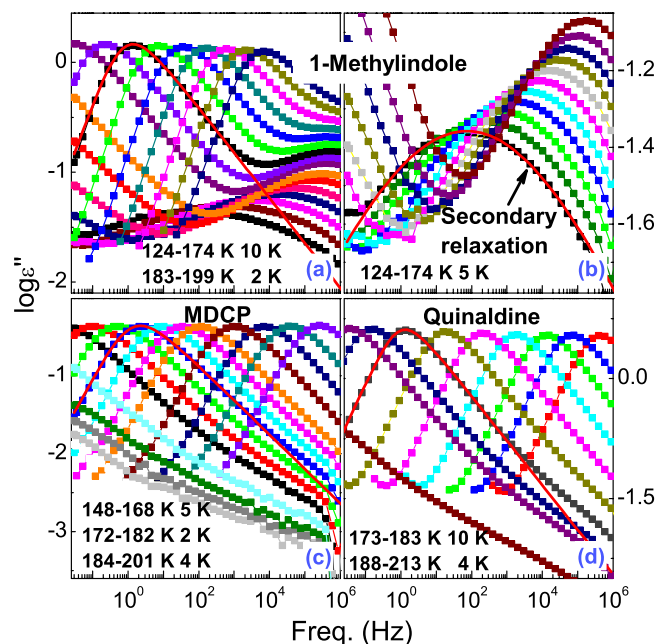


FIG. 2. Frequency dependent dielectric loss ( $\epsilon''$ ) spectra of 1-methylindole (a), MDCP (c), and quinaldine (d) in various temperature ranges. The fits of Havriliak-Negami equation to the loss curves in (a), (c), and (d) are shown. The temperature evolution of the secondary relaxation process of 1-methylindole from 124 to 174 K with step of 5 K is shown in (b), and the red line is the fit curve of Cole-Cole equation. The fitting result of the 1-methylindole at 187 K is marked by the red full line in (a), with  $\Delta\epsilon_\alpha = 5$ ,  $\log_{10}(\tau/s) = -0.6$ ,  $\alpha = 0.92$ ,  $\gamma = 0.44$ . The fitting data of the MDCP at 178 K is shown in (c),  $\Delta\epsilon_\alpha = 1.5$ ,  $\log_{10}(\tau/s) = -0.85$ ,  $\alpha = 0.87$ ,  $\gamma = 0.5$ . And the results of quinaldine at 188 K were fitted previous measurements by Capaccioli in (d), with  $\Delta\epsilon_\alpha = 11.2$ ,  $\log_{10}(\tau/s) = -0.72$ ,  $\alpha = 0.96$ ,  $\gamma = 0.59$ .

and 11.2,  $-0.72$ ,  $0.96$ , and  $0.59$  for QN at 188 K. In contrast to QN and MDCP, the spectra of 1MID reveal a strong and fast  $\beta$ -relaxation on the high-frequency side of the dominant  $\alpha$  loss peak. The frequency dispersion of the  $\alpha$ -relaxation in QN is the most narrow. Fig. 2(b) presents the loss spectra of 1MID measured below the glass transition temperature, and the good fits by the Cole-Cole function, which is typical for secondary relaxation. In contrast, no  $\beta$ -relaxation peak is resolved in the dielectric loss spectra of MDCP (Fig. 2(c)) and QN (Fig. 2(d)) at low temperature.

The reciprocal temperature dependence of the  $\alpha$ -relaxation times of 1MID, QN, and MDCP are shown in Fig. 3. The dielectric glass transition temperature,  $T_g$ , is defined as the temperature at which  $\tau_\alpha$  reaches 100 s. The data of  $\tau_\alpha(T)$  are fitted using the Vogel-Fulcher-Tammann (VFT) equation,  $\log \tau_\alpha = A + B/(T - T_0)$ , where  $A$ ,  $B$ , and  $T_0$  are constants. The kinetic fragility index,  $m = d \log \tau_\alpha / d(T_g/T)_{T=T_g}$ , can thus be calculated from the VFT fit and are shown together with  $T_g$  in Table I. It can be seen that  $T_g$  of 1MID and QN are comparable, 10 K higher than that of MDCP. MDCP and QN have almost the same  $m$  values of 75 and 76, respectively, and comparable to  $m = 80$  for 1MID.

The temperature dependences of the dielectric strengths  $\Delta\epsilon_\alpha$  of the  $\alpha$ -relaxations of the three liquids are shown in the inset of Fig. 3. QN has the highest relaxation strength and MDCP has the lowest value. Dynamic and thermodynamic parameters relevant to glass transition of 1MID, QN, and MDCP are summarized in Table I, where the Kohlrausch

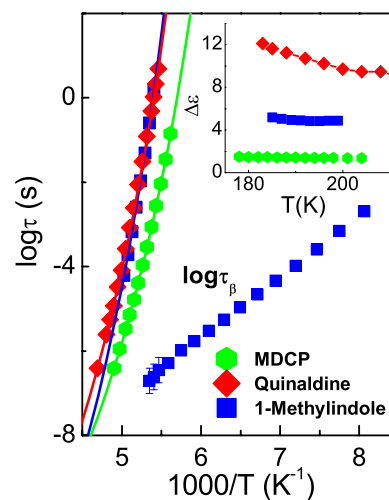


FIG. 3. Temperature dependence of relaxation time of 1-methylindole, MDCP, and quinaldine. The solid lines are the fit of the dielectric data with a VFT function. The temperature dependence of the dielectric strength  $\Delta\epsilon_\alpha$  of the structural relaxation of the three neat molecules is shown in the inset.

non-exponential parameter  $(1 - n)$  is determined from the fits to the  $\alpha$ -loss peak in the  $\epsilon''(f)$  data measured near and above the glass transition temperature by using the one-sided Fourier transform of the KWW function in Eq. (1). Interestingly, 1MID and MDCP have similar values of  $(1 - n)$ , but the secondary relaxations are resolved in 1MID while not in MDCP. The significance of the difference between the MDCP and 1MID will be discussed in Section IV. It is basically due to the larger in-plane dipole moment of 1MID than MDCP.

One can see in Table I, some of the parameters including density of the three liquids are quite similar, however, this does not lead them to have similar properties of their  $\beta$ -relaxations. Consequently, it is relevant to investigate 1MID for the origin of its large dielectric strength and the presence of the resolved intense  $\beta$ -relaxation in it. Secondary relaxations, whether intramolecular or intermolecular in nature, generally have three basic dynamic characteristics: (1) Cole-Cole dielectric dispersion, (2) Arrhenius temperature dependence of the  $\beta$ -relaxation time  $\tau_\beta$  at temperatures below  $T_g$ , and (3) increasing dielectric strength with temperature.<sup>33,38</sup> The reciprocal temperature dependence of the  $\beta$ -relaxation time of 1MID in Fig. 3 shows the Arrhenius dependence below  $T_g$ . The temperature dependence of the  $\beta$ -relaxation strength in Fig. 4(a) shows it increases with temperature. It appears that the dielectric  $\beta$ -relaxation of 1MID have the three basic dynamic characteristics of  $\beta$ -relaxations. However, the molecular origin of this relaxation and that its nature is whether intermolecular or intramolecular has yet to be determined.

For some molecular liquids, the relation of the activation energy  $E_\beta$  of JG  $\beta$ -relaxations to  $T_g$  is approximately given by the relation  $E_\beta = 24RT_g$ ,<sup>36</sup> where  $R$  is the gas constant. The values of  $E_\beta$  of molecular liquids are presented in Fig. 4(b).<sup>19,22,23,39-54</sup> It was noted before that the aforementioned relation of activation energy to  $T_g$  is not universal.<sup>41</sup> Many true JG  $\beta$ -relaxations, not shown in Fig. 4(b), are exceptions to the relation, and also many non-JG intramolecular secondary relaxation obey this relaxation. A spectacular example is the family of oligomeric  $n$ -(propylene glycol)

TABLE I. Thermodynamic and kinetic properties involved in glass formation of 1-methylindole, MDCP, and quinaldine.  $M_w$ ,  $T_b$ ,  $T_m$ ,  $T_g$ ,  $m$ ,  $\beta_{KWW}$ , and  $\rho$  are molecular weight, boiling point, melting point, glass transition temperature, fragility index, non-exponential parameter, and density, respectively.

Materials	Formula	Mw	$T_b$ (K)	$T_m$ (K)	$T_g$ (K)	$m$	$\beta_{KWW}$	$\rho$ (g/cm <sup>3</sup> )
1-Methylindole	C <sub>9</sub> H <sub>9</sub> N	131.2	510	275.56	181	80 ± 5	0.54	1.051
MDCP	C <sub>8</sub> H <sub>10</sub> N <sub>2</sub>	134.2	...	...	170.4	75	0.56	1.055
Quinaldine	C <sub>10</sub> H <sub>9</sub> N	143.2	521	270.3	180	76 ± 6	0.72	1.058

dimethyl ethers with widely different  $T_g$ 's but nearly the same activation energy for the resolved JG  $\beta$ -relaxations.<sup>55,56</sup> The activation energy  $E_\beta$  of 1MID is also shown in Fig. 4(b), and nevertheless it is basically consistent with the rule. The  $E_\beta$  value of 1MID is quite comparable with those of decahydroisoquinoline (DHIQ) and  $\alpha$ -tetralone, which have been proven to be non-JG  $\beta$ -relaxation.<sup>39,57</sup> Therefore, the ratio of activation energy  $E_\beta$  to  $RT_g$  cannot be used as a definitive argument in favor or against the intermolecular nature of the secondary relaxation in 1MID.

The isothermal dielectric loss spectra of toluene, MDCP, QN, and 1MID each normalized by the maximum loss at the  $\alpha$ -loss peak at the same frequency are shown in Fig. 5. The dielectric relaxation data of toluene, a small, rigid, and planar molecule, are selected for comparison, with due consideration of the fact that the well-resolved secondary relaxation in toluene has been proven to be the JG  $\beta$ -relaxation.<sup>20</sup> Significant differences are evident in the high frequency flank of the normalized peaks of the four molecular liquids. The relationships between  $\alpha$ -relaxation and JG  $\beta$ -relaxation times had been established by the CM<sup>7,9,10,58</sup> and are consistent with the results from considerable number of experimental studies in many glass-forming systems.<sup>7,9-12,14,15,17,19-23,27,28,30-33,39,40,44,47,48,53,56,57</sup> One relation showed that the dynamic separation between the  $\alpha$ - and the JG  $\beta$ -relaxations depends on the coupling parameter

$n$  ( $n \equiv (1 - \beta_{KWW})$ ), and it is given by

$$\log \tau_\alpha - \log \tau_{JG} \approx n(\log \tau_\alpha - \log t_c), \quad (3)$$

where  $\tau_\alpha$  and  $\tau_{JG}$  are the  $\alpha$ - and the JG  $\beta$ -relaxation times, and  $t_c$  has approximately the value of 1–2 ps for molecular glass-formers.<sup>7,9,59</sup> The approximate relation (relation (3)) is deduced from the approximate equality,  $\tau_{JG} \approx \tau_0$ , and the exact CM relation,<sup>7</sup>

$$\log \tau_\alpha - \log \tau_0 = n(\log \tau_\alpha - \log t_c), \quad (4)$$

where  $\tau_0$  is the primitive relaxation time in the CM. The comparable values of  $(1 - n)$  for toluene (0.53),<sup>20</sup> 1MID (0.54), and MDCP (0.55) at  $T_g$  mean that for the same relaxation time of the  $\alpha$ -relaxation, a similar timescale  $\tau_{JG}$  for the JG  $\beta$ -relaxation should be expected from relation (3). However, the data of these three glass-formers are apparently at odds with the expectation, as can be seen by comparing them in Fig. 5. The observed peak frequency of the  $\beta$ -relaxation of 1MID is located almost a decade higher than that of toluene and the calculated primitive relaxation frequency  $f_0 \equiv 1/(2\pi\tau_0)$  via Eq. (4). On the other hand, for MDCP, no secondary relaxation loss peak has been resolved, and its  $\tau_{JG}$  cannot be clearly identified.

These findings are quite puzzling, since all the systems considered are rigid molecules, having no intramolecular degrees of freedom. In particular, for 1MID, the absence of intramolecular transitions and different tautomers or conformers has been demonstrated.<sup>60-62</sup> The same applies to both

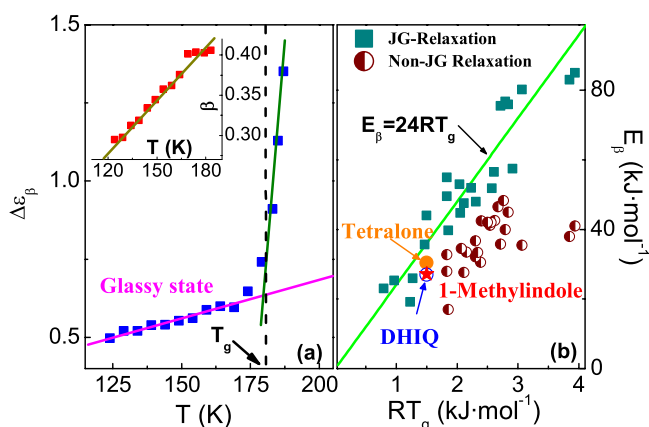


FIG. 4. (a) Temperature dependence of relaxation strength and  $\beta_{Cole-Cole}$  of secondary relaxation in 1-methylindole, and the non-exponential parameter  $\beta_{Cole-Cole}$  is fitted by Cole-Cole function. (b) Dependence of the activation energy for  $\beta$ -relaxation,  $E_\beta$ , on glass transition temperature  $T_g$  for small molecular glass formers. The solid line denotes the average activation energy,  $E_\beta = 24RT_g$ . Semi-closed circles denote the non-JG  $\beta$ -relaxation. The closed squares denote the JG  $\beta$ -relaxation. The lone star denotes the 1-methylindole. The orange filled circle denotes the  $\alpha$ -tetralone. The blue open circle denotes the DHIQ.

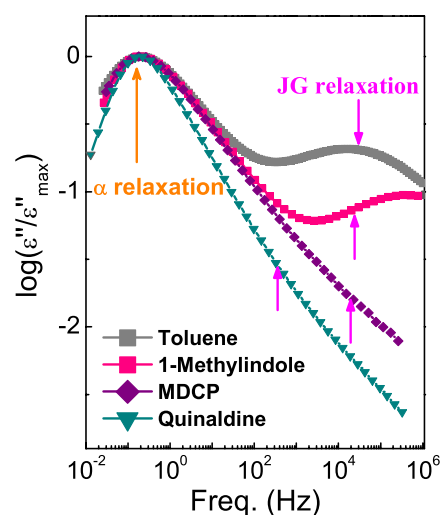


FIG. 5. Normalized dielectric loss ( $\epsilon''$ ) spectra of 1-methylindole at 185 K (square symbols) compared with that of toluene at 121 K (grey line), MDCP at 175 K (diamond symbols), and quinaldine at 185 K (triangular symbols). Slight horizontal shifts have also been applied.

QN and MDCP. Consequently, if the secondary relaxation observed in 1MID was the true JG  $\beta$ -relaxation, it would be in disagreement with the coupling model prediction, and an exception to the rule verified in many other glass-formers. Another problem is that MDCP does not show any resolved JG  $\beta$ -relaxation on the high frequency flank of the  $\alpha$ -relaxation despite the width of the  $\alpha$ -dispersion is about the same as 1MID and toluene. All the experimental data of 1MID and MDCP are seemingly exceptions to the rule, casting doubts on the current understanding of the JG  $\beta$ -relaxation in glass-forming systems. Notwithstanding, we shall demonstrate in Sec. IV that these exceptions found in 1MID and MDCP are caused by the in-plane rotation of these rigid and planar molecules with disparity in the size of the dipole moment. Details of the explanation of the anomalous behaviors of 1MID and MDCP shown in Fig. 5 by the in-plane rotation are given in Sec. IV.

Another possibility of the origin of the intense  $\beta$ -relaxation in 1MID is the fluctuations of H-bonded clusters, if present. This scenario happened before in the dielectric relaxation study of *m*-fluoroaniline (mFA), another rigid molecule.<sup>20,63,64</sup> The strong  $\beta$ -relaxation in mFA is located at much higher frequencies than those predicted by relation (3) and Eq. (4) of the CM with the small value of  $n = 0.38$  of mFA at  $T_g$ . Like 1MID, the data of mFA at first impression are another example of apparent violation of the CM prediction. However, neutron scattering<sup>63</sup> and simulation<sup>64</sup> data showed the presence of hydrogen-bond-induced clusters of limited size in mFA at ambient pressure and temperature of the dielectric measurements. The possibility that the  $\beta$ -relaxation may originate from the hydrogen-bond-induced clusters was confirmed by applying elevated pressure in dielectric measurements.<sup>20</sup> Hence, the  $\beta$ -relaxation in mFA is a non-JG  $\beta$ -relaxation, and its deviation from the CM prediction is natural. Remarkably, after having eliminated the hydrogen-bonded clusters in mFA by elevated pressure and temperature, the  $\alpha$ - and  $\beta$ -relaxations of the modified mFA are nearly identical to those of toluene, and the value of  $\log(\tau_\alpha/\tau_\beta)$  obeys the CM prediction by relation (3).<sup>20</sup>

The temperature dependence of the  $\alpha$ - and  $\beta$ -relaxation times of 1MID is compared with those of mFA and toluene with similar molecular structure in Fig. 6. 1MID has a similar phenyl ring attached to a nitrogen atom as mFA but no N-H group as in mFA, and the H-bond induced clusters might be expected, as observed in the case of mFA. The Fourier transform infrared spectrum of 1MID is presented in Fig. 7. The broad band in the range 3300-2800  $\text{cm}^{-1}$  can be assigned to the stretching vibration of C-H bonds. The peaks at 3050  $\text{cm}^{-1}$  and 2950  $\text{cm}^{-1}$  correspond to the stretching vibration of the unsaturated C-H and saturated C-H. Studies show that when H-bonds forms between a nitrogen atom and a hydrogen atom of another molecules, the peak profile and position of the C-N bonds and C-H bonds would be modified, and the peaks get broadened and move toward lower wave numbers.<sup>65</sup> Hill and co-workers considered that a N-C group attached to or contained in an aromatic system gives a characteristic band between 2820 and 2810  $\text{cm}^{-1}$ ,<sup>66</sup> and the 2816  $\text{cm}^{-1}$  sharp peak with weak intensity seems to be located in the region of N-C stretching vibration. When the group is

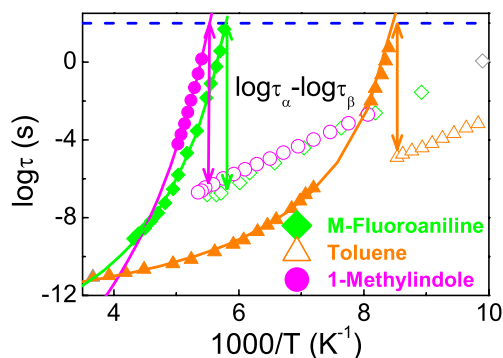


FIG. 6. Dielectric relaxation times of 1-methylindole, mFA and toluene plotted against  $1000/T$ . The solid and open symbols denote the relaxation times of  $\alpha$ - and secondary relaxation, respectively. The dashed lines indicate the relaxation time (100 s) to the  $T_g$ . The arrows indicate the distance between the  $\alpha$ -relaxation and the secondary relaxation.

in an aliphatic (or a non-aromatic heterocyclic) system the band occurs in the 2805-2780  $\text{cm}^{-1}$  range. It is consequently deduced that the formation of H-bonds is frustrated due to the steric effect of the phenyl ring, consistent with the argument that no  $-\text{N}\cdots\text{H}$  moiety is available in 1MID.<sup>67,68</sup> Thus, the  $\beta$ -relaxation in the 1MID does not originate from H-bond-induced clusters as in mFA.

There are other examples of apparent deviation of the relation between  $\tau_\beta$  and  $\tau_\alpha$  predicted by relation (3) of the CM from the first impression of the dielectric relaxation data. One outstanding example can be taken out from the unique and intense secondary relaxation in DHIQ found by Richert *et al.*<sup>69</sup> at atmospheric pressure. Its relaxation time is of orders of magnitude longer than that predicted with the value 0.40 of the stretch exponent  $\beta_{KWW} \equiv (1 - n)$  in the Kohlrausch function that fits the  $\alpha$ -loss peak. If the observed secondary relaxation is the JG  $\beta$ -relaxation, then DHIQ offers a spectacular refutation of the CM prediction. However, experiments performed later by Paluch *et al.*<sup>57</sup> at elevated pressure on DHIQ found that while the  $\alpha$ -relaxation shifts to lower frequencies, the prominent secondary relaxation is insensitive to applied pressure. This shows that the observed secondary relaxation has no connection to the  $\alpha$ -relaxation and incompatible with one of the criteria established to identify secondary relaxation of the Johari-Goldstein kind. Hence, it is not the JG  $\beta$ -relaxation of DHIQ and possibly arises from

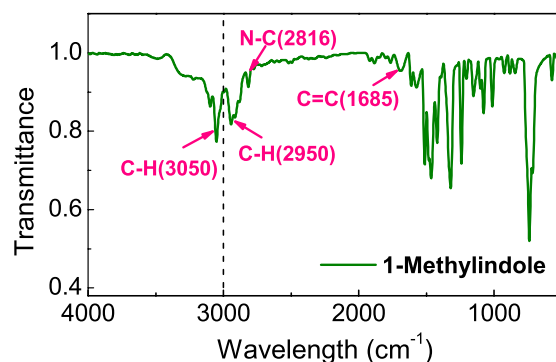


FIG. 7. Infrared spectrum of the 1-methylindole in the 500-4000  $\text{cm}^{-1}$  region.

some conformational interconversion mechanism, reflecting in dipole fluctuations. The genuine JG  $\beta$ -relaxation of DHIQ with much weaker dielectric strength was found in the glassy state at the high frequency end of the non-JG secondary relaxation.<sup>57</sup>

The examples from mFA and DHIQ point out that the sole resolved secondary relaxation is not the genuine JG  $\beta$ -relaxation. Additional experiments at elevated pressure had to be performed to show it is pressure insensitive and hence not the JG  $\beta$ -relaxation. There are many such examples including diethyl phthalate (DEP),<sup>70</sup> di-*n*-butyl phthalate (DBP),<sup>71</sup> benzophenone,<sup>28,72</sup> and benzyl acetate.<sup>73,74</sup> The true JG  $\beta$ -relaxation is unresolved in any of these glass-formers, but its existence was confirmed in mixtures of these glass-formers with a less mobile apolar component.<sup>28,74</sup>

There is the danger of mistakenly identifying the observed non-JG secondary relaxation as the JG  $\beta$ -relaxation. Naturally, its relaxation time does not satisfy the CM prediction. Nevertheless, this result could be misused to contradict the CM prediction. Thus, before jumping to conclusion that the observed secondary relaxation in 1MID is the JG  $\beta$ -relaxation and it violates relation (3) of the CM as evident in Fig. 5, additional experiment has to be performed to ascertain its identity. This requirement leads us to consider further the origin of the secondary relaxation of 1MID in Sec. IV and mention some preliminary experiments to confirm that it is not the JG  $\beta$ -relaxation.

#### IV. RESOLUTION OF THE ANOMALIES

The results given in Sec. III have revealed the contrasting dynamic properties of the  $\alpha$ - and  $\beta$ -relaxations in 1MID, MDCP, and toluene. Despite all the three glass-formers are rigid and planar molecules, and the widths of the  $\alpha$ -loss peak or the Kohlrausch non-exponentiality exponents,  $\beta_{KWW} \equiv (1 - n)$ , have comparable values, both the relaxation time  $\tau_\beta$  and dielectric strength  $\Delta\epsilon_\beta$  relative to the corresponding quantities of the  $\alpha$ -relaxation are very different. The findings in 1MID and MDCP are at variance with the general behavior established empirically in many glass-formers and binary mixtures.<sup>9-11,15,21,36,75,76</sup> The data of 1MID and MDCP seemingly contradict the prediction of relation (3) in the CM, while toluene conforms to it as shown before.<sup>20</sup> To explain these anomalies, first we point out the in-plane dipole moment from the N-C bond in 1MID is significantly larger than that in MDCP and toluene. 1MID not only has a large in-plane dipole moment but also different sizes of the two adjacent rings, the aromatic one and the 5-member ring with nitrogen having the methyl group attached to it. This could favor local in-plane rotations and rearrangements of the molecule. Therefore, the in-plane rotation of 1MID gives rise to a strong secondary relaxation, which is basically not observable in MDCP and toluene. Notwithstanding, this strong secondary in-plane relaxation is not the JG  $\beta$ -relaxation in 1MID, which is contributed by out-of-plane rotation of the 1MID and MDCP. This is because in-plane rotation is an isolated or independent process not effective to induce intermolecular coupling, and therefore it bears no connection to the intermolecularly coupled or cooperative  $\alpha$ -relaxation. On one hand, out-of-plane rotations cause intermolecular

coupling and become the precursor of the  $\alpha$ -relaxation, which is the characteristic of the JG  $\beta$ -relaxation.<sup>14</sup>

On the other hand, the in-plane dipole moment of MDCP is small and the dielectric strength of the in-plane rotation is negligible. Actually, the 3D structure of MDCP does show a slight non-planarity, with a puckering of the 5 member carbon rings with a methyl group attached.<sup>77</sup> The non-perfectly planar structure could hinder in-plane rotation and reduce its relaxation strength. Hence, the prominent  $\beta$ -loss peak originating from in-plane rotation of 1MID is absent in the loss spectra of MDCP. This situation in MDCP makes possible for the appearance of a change of curvature of  $\epsilon''(f)$  at frequencies several decades higher than the  $\alpha$ -loss peak. This feature in the spectra is the vestige of the unresolved JG  $\beta$ -relaxation in MDCP and its time scale is consistent with the CM prediction to be shown later.

Actually, with the methyl group attached to the nitrogen atom in 1MID, the electron density changes in the vicinity of the ring nitrogen atom and this could cause rotation-vibration coupling and then change in overall in-plane orientation of the rotational axes. So, the possibility of a fast reorientational mechanism in 1MID cannot be completely ruled out. Similar arguments could be used for MDCP. However, what needs to be addressed is that albeit the  $n$  values and rigidity for 1MID and MDCP are comparable, a marked difference in the secondary relaxation is obvious. If an in-plane rearrangement does occur in 1MID, the nitrogen atom must be a significant factor in enhancing the dielectric strength of the secondary relaxation. In contrast, a similar mechanism in MDCP is not present in its less polar carbon ring, and so the in-plane rotation does not contribute to a resolved  $\beta$ -relaxation.

The points made so far are brought out in Fig. 8, where a closer examination of the loss data of 1MID in Fig. 2 at temperatures above  $T_g$  is compared with toluene at one temperature. The shifts of the  $\beta$ -loss peak frequency,  $f_{\beta p}$ , of 1MID are traced exactly by the thick black line, which indicates a change of  $f_{\beta p}$  by only 0.4 decade over the four temperatures shown in Fig. 8. On the other hand, the corresponding change of the  $\alpha$ -loss peak frequency,  $f_{\alpha p}$ , is 3.4 decades, in the same temperature range. The exceedingly

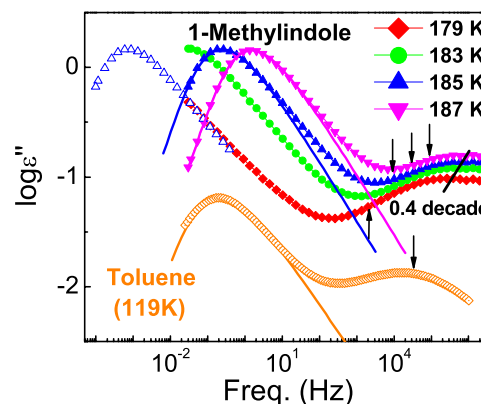


FIG. 8. Dielectric loss ( $\epsilon''$ ) spectra of 1-methylindole at 179 K, 183 K, 185 K, and 187 K and toluene at 119 K. The hollow triangle is the shift of the dielectric data with a KWW function. The arrows indicate the frequency of relaxation peaks of JG  $\beta$ -relaxation for 1-methylindole.

large disparity between  $f_{\beta p}$  and  $f_{\alpha p}$  in the magnitudes of the shifts with temperature is foretelling that the relaxation responsible for the  $\beta$ -peak is somehow unrelated to the  $\alpha$ -relaxation, and hence it might not be the JG  $\beta$ -relaxation of 1MID. The disparity is obviously inconsistent with the CM prediction by relation (3). This can be seen from the JG  $\beta$ -relaxation frequencies,  $f_{JG} \equiv 1/(2\pi\tau_{JG})$ , estimated by the primitive frequency,  $f_0 \equiv 1/(2\pi\tau_0)$ , with  $\tau_0$  calculated via Eq. (4) with  $n = 0.45$  determined from the fits to the  $\alpha$ -loss peak of 1MID by the Fourier transform of the Kohlrausch function. The calculated  $f_0$  for each of the four temperatures in Fig. 8 is indicated by the vertical arrows. The shift of  $f_0$  and approximately  $f_{JG}$  over the temperature range in Fig. 8 is 1.8 decades, which is 4.5 times the shift of  $f_{\beta p}$  of the resolved  $\beta$ -loss peak. Also evident by inspection of Fig. 8 is the proximity of  $f_{JG} \approx f_0$  to  $f_{\beta p}$ . This suggests that the JG  $\beta$ -relaxation of 1MID is dominated by the intense non-JG  $\beta$ -relaxation and explains why it is not resolved.

The dipole moment of toluene lies in the plane of the molecule. Its small value is evidenced by the low loss  $\epsilon''(f)$  of both of the  $\alpha$ - and JG  $\beta$ -relaxations in Fig. 8 compared with 1MID. The logarithm of the maximum loss at the JG  $\beta$ -relaxation peak frequency  $f_{JG}$  has the value of  $\log[\epsilon''(f_{JG})] = -1.86$ . As discussed in Sec. III, MDCP has small in-plane dipole moment like toluene. Therefore, the in-plane rotation of these two rigid molecules does not contribute any significant loss and hence the non-JG  $\beta$ -relaxation found in 1MID is not observed in MDCP and toluene. The absence of the intense non-JG  $\beta$ -relaxation in MDCP makes possible the detection of its JG  $\beta$ -relaxation in the spectra. In Fig. 9, we reproduce the dielectric loss data of MDCP at a few temperatures near and above  $T_g$ . Remarkably, near the loss at the level of  $\log(\epsilon'') = -2$ , we find apparent change in the curvature of  $\log(\epsilon''(f))$  as a function of  $\log f$ . This change is elucidated by the pair of intersecting broken lines constructed for two temperatures as examples, and it gives indication of the presence of the unresolved JG  $\beta$ -relaxation in MDCP with its relaxation frequency  $f_{JG}$  near the intersection. The Kohlrausch fits of the  $\alpha$ -loss peaks in Fig. 9 determines  $n = 0.44$ . The  $f_0 \equiv 1/(2\pi\tau_0)$ , calculated via Eq. (4) is about 1 decade higher than the frequency at which the curvature of  $\log(\epsilon''(f))$  changes. This order of magnitude agreement between  $f_0$  and the purported location of  $f_{JG}$  is in accord with the approximate equality,  $\tau_{JG} \approx \tau_0$ , and relation (3) of the CM, and it lends another support to the presence of the unresolved JG  $\beta$ -relaxation in MDCP. It is worthwhile to point out that although MDCP and toluene has comparable relaxation dispersion, or  $\beta_{KWW}$ , the relative intensity of their  $\alpha$ - and JG  $\beta$ -relaxation differs substantially. The dielectric strength of the JG  $\beta$ -relaxation depends on the amplitude of the angle of rotation of the molecule, which in turn depends on the physical and chemical structures of the molecule, steric constraints, and packing density. Smaller size of the less polar toluene may allow larger angle of rotation than MDCP. Also MDCP has the methyl group sticking out of the plane and it can restrict the amplitude of rotation. On the other hand,  $\alpha$ -relaxation is responsible for viscous flow, and rotation of molecules is not restricted in amplitude because rotation is coupled to translation in flow. This difference between the

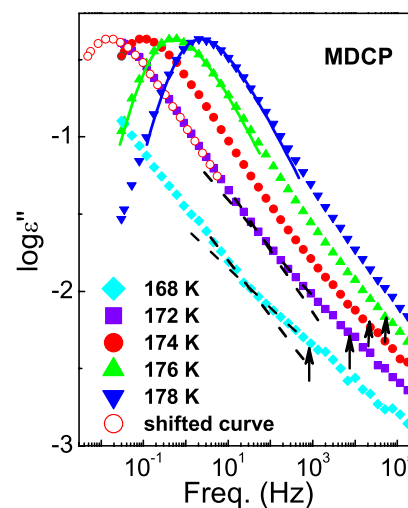


FIG. 9. Dielectric loss ( $\epsilon''$ ) spectra of MDCP at 179 K, 183 K, 185 K, and 187 K. The arrows indicate the frequency of relaxation peaks of JG  $\beta$ -relaxation for MDCP. The solid lines are the fit of the dielectric data with a KWW function. The hollow circle is the shift from the 174 K. The dashed lines show the change in the curvature of  $\log(\epsilon''(f))$  as a function of  $\log f$ .

$\alpha$ -relaxation and the JG  $\beta$ -relaxation together with the factors given above may account for the much lower strength of the latter relative to the former in MDCP than toluene.

For the sake of completeness, we also consider the difference between QN and 1MID. Although both rigid molecules have one nitrogen in the ring, the methyl group is attached to the carbon in QN, but instead to the nitrogen in 1MID. These two notable differences in structure between these two rigid glass-formers can account for the larger dipole moment in 1MID than in QN, and this is one factor making the non-JG relaxation from in-plane rotation of QN not observed. Additionally, there is a difference in the strength of intermolecular coupling between QN and 1MID. This difference can be inferred from the much narrower  $\alpha$ -loss peak of QN than 1MID corresponding to smaller coupling parameter  $n = 0.28$  of QN than  $n = 0.46$  of 1MID (see Table I). The primitive relaxation time  $\tau_0$  of QN calculated by Eq. (4) is much closer to the dominant loss peak of QN (see Fig. 5), and that is the reason why the JG  $\beta$ -relaxation of QN cannot be resolved, like in many similar cases from other glass-formers. The in-plane rotation and the primitive relaxation are both independent modes of relaxation, and their relaxation times should be close to each other. Thus, following the primitive relaxation, the secondary relaxation contributed by the in-plane rotation of QN is also located too close to the dominant  $\alpha$ -relaxation and cannot be resolved.

The explanations of the anomalies found in 1MID and MDCP given above can be further tested by experiments currently underway and more planned to be executed in the near future. The objective is to observe the changes of the  $\alpha$ - and  $\beta$ -relaxations in 1MID and MDCP by either mixing with another glass-former or by applying elevated pressure. The effects on the in-plane rotational relaxation and the unresolved JG  $\beta$ -relaxation of 1MID are expected to be different. If observed, the different effects on the two relaxations can separate them out to reveal the JG  $\beta$ -relaxation of 1MID either in the mixture or in the bulk under elevated pressure. Preliminary



results have been obtained from dielectric measurements of the change of the  $\alpha$ - and  $\beta$ -relaxations of the polar 1MID component in mixtures with either apolar ethylbenzene or triphenylethylene having lower and higher  $T_g$  than 1MID, respectively. While there are many orders of magnitude decrease of the  $\alpha$ -relaxation time of the 1MID component in mixtures with ethylbenzene and increase in mixtures with triphenylbenzene, the  $\beta$ -relaxation times in these mixture are the same as in neat 1MID. The result indicates that the  $\beta$ -relaxation of 1MID bears no connection to the  $\alpha$ -relaxation, and definitely it is not the JG  $\beta$ -relaxation. The findings from the mixtures of 1MID and MDCP with ethylbenzene and triphenylbenzene will be reported elsewhere in the near future. The effects by mixing with ethylbenzene or triphenylethylene on MDCP will be different due to the absence of the contribution to  $\varepsilon''(f)$  from the in-plane rotational relaxation.

## V. CONCLUDING REMARKS

Experimental studies of primary and secondary relaxations of rigid molecular glass-formers in the pure state and not in mixtures are rare. Many rigid molecular glass-formers are prone to crystallization and not amenable for study. For those few ones that have been studied including QN and 2-picoline, the  $\alpha$ -relaxation has narrow frequency dispersion and no secondary relaxation can be resolved. The few exceptions are toluene, and mFA under high pressure and temperature to remove the hydrogen-bonded clusters. We have introduced two new rigid molecular glass-formers, 1MID and MDCP, which can be supercooled and studied in the liquid and glassy states. The properties of the  $\alpha$ -relaxation and the secondary relaxation are strongly connected if the secondary relaxation is of the Johari-Goldstein kind as verified by experiments in many glass-formers and mixtures. Our effort is rewarded by finding the dynamics in 1MID and MDCP are very different from toluene, quinaldine, and 2-picoline. 1MID and MDCP are rigid and planar molecules like the others, and yet the properties are so different. While the dynamics of toluene, QN, and 2-picoline are in accord with the empirical relation between the  $\alpha$ - and JG  $\beta$ -relaxations established in many glass-formers and conform to the predictions of the CM, the anomalous properties found in 1MID and MDCP pose difficulty to explain why these molecules behave so differently.

After having eliminated other causes including hydrogen-bonding, we trace the origin of the anomalous secondary relaxation of 1MID to the in-plane rotation which is observable due to the asymmetric structure and large dipole moment on the plane of the molecule. This non-JG secondary relaxation eclipses the slower and weaker JG  $\beta$ -relaxation in the dielectric loss spectra and is the cause of the anomalous property when it is identified erroneously as the JG  $\beta$ -relaxation. The difference of MDCP from 1MID is due to the significantly smaller in-plane dipole moment of MDCP. Consequently, the non-JG secondary relaxation contributed by the in-plane rotation is absent in the loss spectra of MDCP, and this accounts for the difference from 1MID. Without the interference from non-JG secondary relaxation, the presence of the JG  $\beta$ -relaxation of MDCP is supported by a fine structure found in the loss spectra at several temperatures. Thus, the relation between the JG  $\beta$ -

relaxation time and the  $\alpha$ -relaxation time of MDCP is basically the same as toluene and is consistent with the CM prediction. QN has a non-negligible in-plane dipole moment albeit smaller, and the in-plane rotation of QN should contribute the non-JG secondary relaxation like in 1MID. The reason that it is not seen in QN is due to the much narrower frequency dispersion of its  $\alpha$ -relaxation or smaller coupling parameter  $n$ . As found before in many glass-formers with small  $n$ , the JG  $\beta$ -relaxation lies too close to the dominant  $\alpha$ -loss peak and cannot be resolved. The non-JG secondary relaxation from in-plane rotation of QN is an independent relaxation like the JG  $\beta$ -relaxation, and hence their relaxation times are comparable. Consequently, both relaxations are too close to the intense  $\alpha$ -relaxation and cannot be resolved. By mixing 1MID with other glass-formers or by applying pressure, it is expected that the effects on the non-JG secondary relaxation from in-plane rotation would be different from the unresolved JG  $\beta$ -relaxation in 1MID. If carried out, these experiments are capable of proving or disproving our explanation. Our preliminary results of the mixtures of 1MID with ethylbenzene and triphenylethylene basically validate the present explanation.

## ACKNOWLEDGMENTS

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