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Reply to 'Comment on "Understanding the infrared spectrum of the protic ionic liquid [DEMA][TfO] by atomistic simulations"' by J. Joo and A. L. East, *Phys. Chem. Chem. Phys.*, 2026, 28, DOI: 10.1039/D5CP02379C

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Joo and East have recently published a Comment on our article (F. Parisi et al., *Phys. Chem. Chem. Phys.*, 2024, 26, 28037, <https://doi.org/10.1039/D3CP06047K>). The Comment is based on the wrong assumption that we misassigned the infrared spectrum of liquid diethylmethylammonium triflate [DEMA][TfO]. The authors incorrectly claim that our hypothesis was that the two bands are due to the NH stretch mode in two different ion-pair structural types. We clarify here that our original analysis did not invoke two separate, static ion-pair structures, but rather a continuum of dynamically evolving hydrogen-bonding environments that naturally produce a broadened, bimodal band shape. The results presented in our paper are aligned with the ones presented in the Comment. The Comment brings up the concept of Fermi resonance, which indeed gives a plausible explanation of the features seen in the experimental absorption spectra.

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In their Comment, Joo and East wrote about our results that “*Their fresh hypothesis was that the two bands are due to the NH stretch mode in two different ion-pair structural types, ...*” This does not correctly reflect our conclusions. In Section 4 (Conclusions) of our article¹ we wrote: “*The continuous shifting of the shared hydrogen atoms' vibrational frequencies over time is caused by a dynamically changing environment around the N–H group. This dynamic environment prevents the IR spectrum's high-frequency region from showing two narrow peaks, which would typically be expected for the N–H stretching mode in two distinct environments. Instead, there is a broadening into two peak-like features at approximately 2800 cm⁻¹ and 3200 cm⁻¹. The broadening arises from distributions of local different environments with different configurations between DEMA and TfO.*” Thus, our interpretation was not based on two distinct, static ion-pair structural types, but on a dynamical distribution of local environments that gives rise to a broadened, bimodal band

shape. Importantly, neither the AIMD results presented in our work nor those shown in the Comment support the existence of two distinct, long-lived ion-pair configurations.

To answer the first point made by Joo and East, we now turn to the number and nature of the peaks in the AIMD spectrum. In our original discussion we referred to two main spectral contributions, centered around ~2800 cm⁻¹ and 3200 cm⁻¹. In the AIMD spectrum, the two peaks are accompanied by an additional feature, which may be interpreted as a “third” peak. As stated in Section 3.4 of the manuscript,¹ this finer structure arises because of the limited system size (10 ion pairs) and trajectory length (60 ps), combined with contributions from vibrations of the methyl and ethyl groups in the same frequency region: “*The second peak we refer to is labelled as 'peak 2' in Fig. 6(a) and represents a broader feature at ~3200 cm⁻¹. It consists of two minor 'peaks', because of the contribution of H_c atoms, intensity of which is severally overestimated by AIMD, and the reduced size of the system.*” In other words, the apparent third peak is not evidence for a separate, well-defined structural motif, but rather a numerical and sampling artifact superimposed on the two main contributions, also influenced by the known tendency of DFT to overestimate the intensity of CH related vibrations.^{2–5}

To answer the second point made by Joo and East, Fig. 1 shows the vibrational density of states (VDOS) of the H–N

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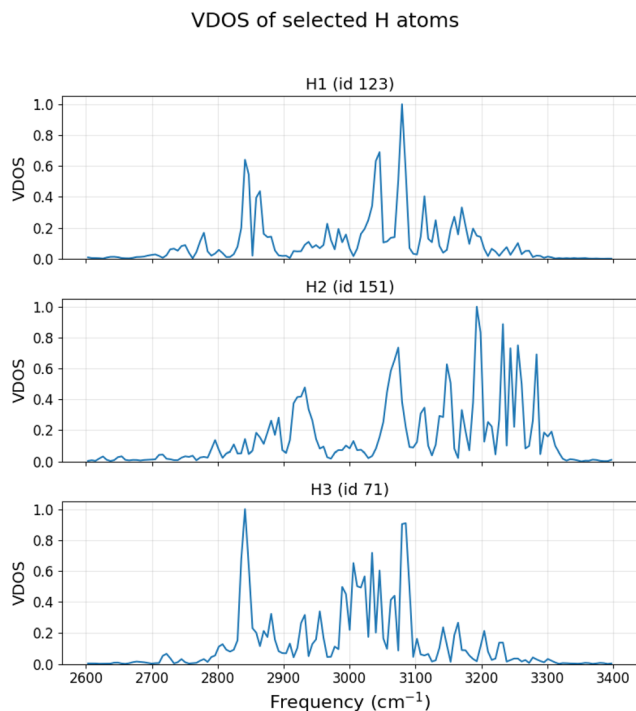


Fig. 1 Vibrational density of states of three different hydrogen atoms (H1, H2 and H3) bonded to nitrogen for three selected cations in the high frequency region. The different values for the “id” are reported in order to easily find them again the molecular dynamics run.

vibration, made by reproducing Fig. 7 of our original manuscript¹ by selecting only three cations and a shorter time. Each VDOS is shown in a separate subfigure in order to improve the visibility. In the plot, we can clearly see vibrations occurring at frequencies higher and lower than 3000 cm⁻¹.

Our work¹ thus shows that hydrogen atoms that exhibit maxima in both regions (*i.e.* below and above 3000 cm⁻¹) clearly experience environments that change over time. In particular, these hydrogen atoms are affected by rotations of the triflate anion: during the simulation, the environment of a given N–H proton switches between configurations analogous to (a) and (b) in Fig. 9 in our manuscript,¹ corresponding to a bending motion of the N–H group as the relative NH...O geometry evolves. This behavior is reflected in Fig. 10 of the manuscript,¹ where the NH–O angle distribution is continuous and can be interpreted as the superposition of two partially overlapping Gaussian-like contributions. The continuity of the distribution stems from the constantly changing local environments and highlights the importance of bending motions as well as stretching.

This interpretation is further supported by the time evolution of the angles discussed in the supplementary information (Section 2.4), where we wrote: “*Together with the high variation in time of the angles, it suggests that the anion undergoes partial rotation throughout the trajectory. This rotational movement further emphasizes the complex and dynamic environment in which these molecular interactions occur*”. The splitting and broadening of the high-frequency band therefore arise from a combination of different

vibrational modes in a fluctuating hydrogen-bonding network, rather than from two rigidly defined structural families.

In their Comment, Joo and East present radial distribution functions of N–H bond-length that evolve towards a single-peak distribution, which they correctly use to argue against two well-separated, long-lived N–H bond-length populations. It is obvious that these data do not support a picture of two static, discrete N–H bond-length states and the analysis presented in Parisi *et al.*¹ does not rely on such a picture. Instead, we emphasize a continuum of dynamically interconverting local environments, characterized by coupled stretching and bending motions and by anion reorientation. In this sense, the structural analysis presented in the Comment is compatible with our original results and conclusions.

We acknowledge Joo and East for suggesting the concept of a “Fermi resonance” as a possible mechanism for features seen in N–H vibrations of cations in complex surroundings. As shown in the references they cite (ref. 6–9), Fermi resonances typically involve coupling between stretching fundamentals and bending overtones or combination bands. These studies indicate that a full description of Fermi resonance requires not only information on bond distances, angular distribution and mode couplings, which we provide in our original paper (Fig. 7–10), but also an explicit treatment of anharmonic mode couplings and nuclear quantum effects. While our original paper provides detailed information on dynamical fluctuations of the hydrogen-bonding environment, it does not explicitly model nuclear wavefunction mixing or anharmonic coupling. The comment by Joo and East also does not provide this information. Therefore, the explanation of the results as “Fermi resonance” requires further studies.

In summary, our original work¹ and the Comment by Joo and East are fully consistent in rejecting a picture based on two static ion-pair configurations. While Fermi resonance represents a plausible mechanism that may contribute to the observed IR band shape, neither study provides any direct computational or experimental proof of its role in the specific case of [DEMA][TfO]. Elucidating this aspect would require dedicated anharmonic vibrational calculations or nuclear quantum treatments, which lie beyond the scope of our studies but remain a challenging task for future research. The primary purpose of this Reply is to clarify the misinterpretation of the conclusions of our original paper by the Comment.

Conflicts of interest

There are no conflicts to declare.

Data availability

All the data are included in this Reply to the Comment.

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