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VIP Ion Pairs

Can Hindered Intramolecular Vibrational Energy Redistribution Lead to Non-Ergodic Behavior of Medium-Sized Ion Pairs?**

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Dedicated to Professor Zdeněk Havlas

Ergodicity, that is, the ability to predict the behavior of an ensemble from the behavior of its components, is a key concept in various areas of science, while in daily life non-ergodic behavior is quite common. In chemistry, ergodicity is typically associated with energy partitioning at a molecular level.[1] Given the selective excitation of a certain rovibrational mode, for example, it is generally assumed that intramolecular vibrational energy redistribution (IVR)[2] is much faster than interactions with the environment. Chemical systems are hence generally assumed to behave ergodically, that is, their properties and in particular their reactivities do not depend on the way of activation, but only on the total energy content, irrespective of the initial state.[3] In turn, non-ergodic behavior refers to chemical systems in which the outcome of a reaction is determined by the initial conditions. Most known examples for non-ergodic behavior in chemistry involve systems containing very few atoms,[4,5] and even systems only slightly larger (e.g. ionized acetone)[6] typically behave ergodically. In recent years, however, electron-capture induced dissociation (ECID) of biomolecules, that is, the recombination of an electron with a multiply charged cation, has been proposed to involve highly excited states of the charged-reduced species, whose dissociations are fast and may not follow ergodicity.[7,8] Similar arguments have been put forward for highly exothermic electron-transfer reactions between dications and neutral molecules[9] or rapid dissociation/abstraction reactions.[10,11] However, for thermal reactions of medium-sized molecules, not only associated with the cleavage of existing, but also with the formation of new chemical bonds, many chemists (including ourselves) would generally deny a non-ergodic behavior.

In the context of possible correlations between gaseous ions and condensed-phase properties,[12] we recently identified a case which challenges the general assumption of ergodic behavior. Specifically, we investigated the noncovalent ion pairs of a triflate ion ($\mathrm{TfO^- = CF_3SO_3^-}$) with a bispyridinium ion that exists in two separable conformers (see structures in Figure 1), which have been termed as helquat (h-$\mathbf{1}^{2+}$) and saddlequat (s-$\mathbf{1}^{2+}$), respectively.[13] Amongst a series of other mass spectrometric studies, we have recorded the infrared-multiphoton dissociation (IRMPD) spectra[14] of the mass-selected ion pairs [h-$\mathbf{1}^{2+}\cdot\mathrm{TfO^-}$] and [$s$-$\mathbf{1}^{2+}\cdot\mathrm{TfO^-}$]. The exclusive fragmentation in IRMPD is a loss of triflic acid through a kinetically controlled Hofmann elimination and is thus associated with the formation of an O−H bond.[15] Surprisingly, the IRMPD spectra do not agree with either the experimental IR spectra of the solid salts [h-$\mathbf{1}^{2+}\cdot 2\,\mathrm{TfO^-}$] and [$s$-$\mathbf{1}^{2+}\cdot 2\,\mathrm{TfO^-}$], respectively, or the computed IR spectra of the singly charged, binary ion pairs [h-$\mathbf{1}^{2+}\cdot\mathrm{TfO^-}$] and [$s$-$\mathbf{1}^{2+}\cdot\mathrm{TfO^-}$] (Figure 1). Favorable agreement is obtained, however, if only the S=O stretching modes (scaling factor 1.0325)[16] are allowed to be active in IRMPD. In this respect it is important to realize that IRMPD is an action spectroscopy, in which the infrared absorption of a gaseous ion is monitored through the amount of fragmentation induced. While this may lead to significant discrimination of certain modes,[17] a situation as profound as in Figure 1, that is, the practical absence of all modes other than certain heteronuclear stretches, has not been addressed before.

One possible explanation for the exclusive response of the S=O modes to the infrared irradiation in the IRMPD experiments is a non-ergodic behavior of the ion pairs [h-$\mathbf{1}^{2+}\cdot\mathrm{TfO^-}$] and [$s$-$\mathbf{1}^{2+}\cdot\mathrm{TfO^-}$]. Thus, the hypothesis is that the S=O bands experience limited intramolecular vibrational energy redistribution (IVR) with the other modes of the molecule such that the triflate unit “overheats”, until proton abstraction becomes kinetically feasible. In turn, adsorption of IR photons in the organic backbone is associated with rapid IVR and hence dissipation of the excess energy across the molecule. While the argument involving non-ergodicity appears fascinating, a problem is that—much like with other

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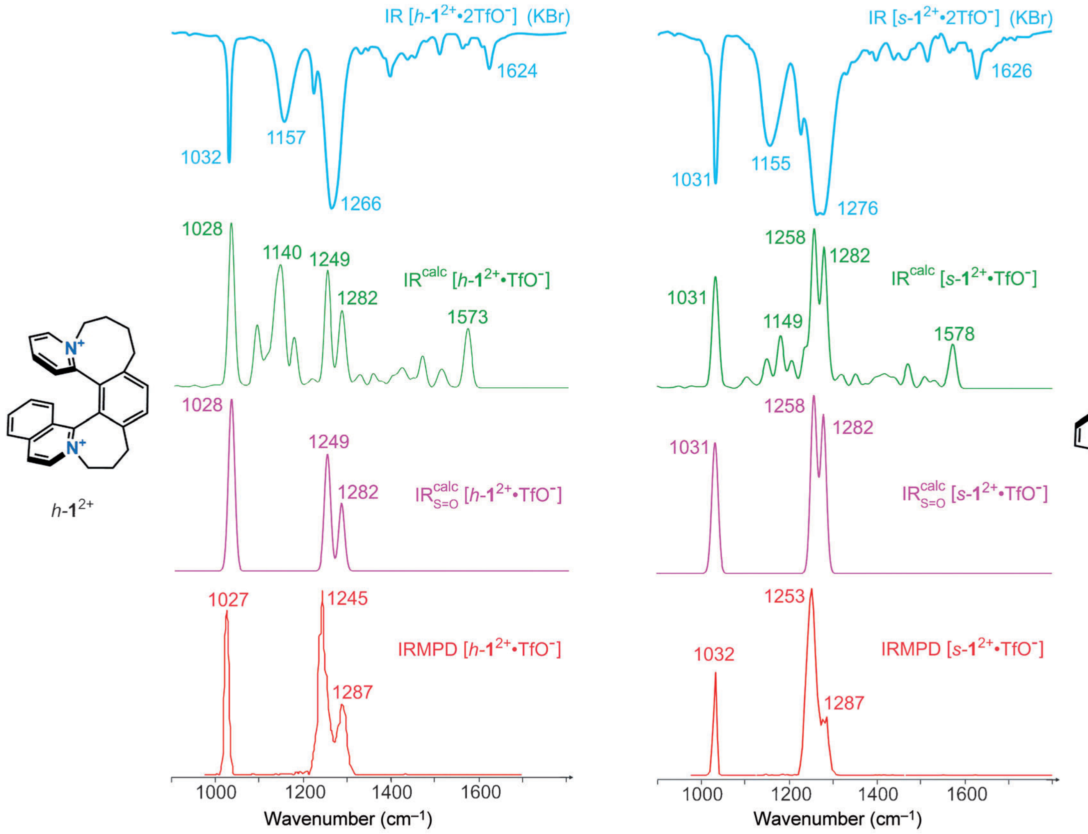

Figure 1. IR spectra of two conformers of a bispyridinium ion with triflate counterions in the range from 900 to 1800 cm^{-1}. Left panel (from the top): Experimental IR spectrum of the solid salt [*h*-$\mathbf{1}^{2+}\cdot 2\,\mathrm{TfO}^-$] (blue), computed IR spectrum of the binary ion pair [*h*-$\mathbf{1}^{2+}\cdot \mathrm{TfO}^-$] (green), S=O bands of the computed IR spectrum of the binary ion pair [*h*-$\mathbf{1}^{2+}\cdot \mathrm{TfO}^-$] (B3LYP/6-311+G(2d,p); pink), and experimental IRMPD spectrum of mass-selected [*h*-$\mathbf{1}^{2+}\cdot \mathrm{TfO}^-$] (red). Right panel: Analogous series for the saddle conformer *s*-$\mathbf{1}^{2+}$.

phenomena which go beyond accepted conventions—many may accept it as a rationale, although it initially remains vague in several respects. For example, the observations in Figure 1 can also be explained by a particularly effective IVR of the S=O modes such that exactly these modes preferentially heat the ion pairs and hence trigger dissociation, whereas the other modes remain invisible because their IVR is insufficient to allow the deposition of a sufficient amount of energy to provoke dissociation.

Accordingly, let us make a thought experiment based on the assumption that the unexpected IRMPD spectra in Figure 1 were due to non-ergodic behavior. If this is not just a peculiarity of the admittedly unusual molecules *h*-$\mathbf{1}^{2+}$ and *s*-$\mathbf{1}^{2+}$, it should be possible to reproduce it for other systems. The above explanation involving non-ergodicity is based upon incomplete IVR of the triflate modes with the organic backbone, where the backbone serves as an energy sink in which the energy is dissipated in multiple modes rather than triggering dissociation. The non-ergodic behavior—if existing at all—should hence be related with the size (i.e. the density of states) of the components "active" and "inactive" with regard to IVR. In this context, the noncovalent nature of the bonding in ion pairs appears to be important. Accordingly, we tested the hypothesis for simple triple ions[18] derived from tetraalkylammonium salts,[19] that is, $[(\mathrm{R_4N^+})(\mathrm{A^-})(\mathrm{R_4N^+})]$ with R = Me and *n*Bu and A = TfO, $\mathrm{ClO_4}$, and AcO. In the respective IRMPD experiments, the corresponding ammonium ions $\mathrm{R_4N^+}$ are the only ionic fragments observed.

The IRMPD spectrum of $[(\mathrm{Me_4N^+})(\mathrm{TfO^-})(\mathrm{Me_4N^+})]$ shows five bands within the spectral regime studied (Figure 2a), whose positions and abundances agree reasonably well with the IR spectrum predicted by density functional theory (DFT).[20] In the following discussion, we focus on the band at about 1280 cm^{-1}, which is characteristic for the S=O stretching, and those close to 1500 cm^{-1}, which correspond to the $\mathrm{CH_2}$ bending modes. For the mixed triple ion $[(\mathrm{Me_4N^+})(\mathrm{TfO^-})(n\mathrm{Bu_4N^+})]$, a similar pattern is observed, although the intensity of the IMRPD band at 1490 cm^{-1} is lower than the theoretically predicted mode at 1497 cm^{-1} (Figure 2b). As striking as the spectra in Figure 1 is the situation for the triple ion with two "large" alkylammonium ions, that is, $[(n\mathrm{Bu_4N^+})(\mathrm{TfO^-})(n\mathrm{Bu_4N^+})]$ (Figure 2c). While the computed IR spectrum is very similar to those of the two other triple ions, the corresponding IRMPD is largely dominated by the S=O modes centered at 1277 cm^{-1}. While three other modes are observed in the IRMPD spectrum, whose positions agree reasonably well with the computed values, their intensities are much lower than those predicted by theory. Particularly, the methylene bending band at 1481 cm^{-1} is almost completely suppressed and only observed in the experimental data upon

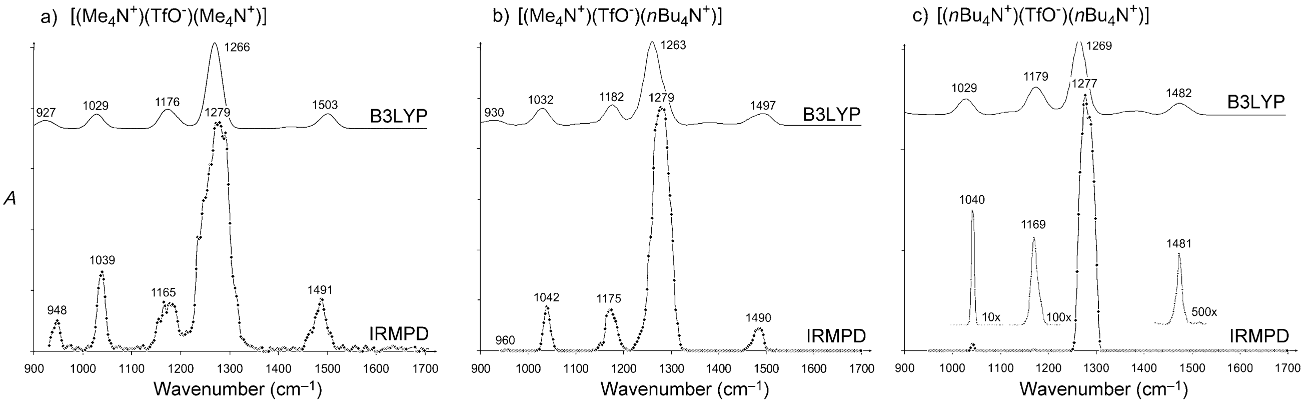

Figure 2. Experimental IRMPD spectra of the mass-selected triple ions a) [(Me$_4$N$^+$)(TfO$^-$)(Me$_4$N$^+$)], b) [(Me$_4$N$^+$)(TfO$^-$)(nBu$_4$N$^+$)], and c) [(nBu$_4$N$^+$)(TfO$^-$)(nBu$_4$N$^+$)] in the range from around 900 to 1700 cm^{-1}. The upper traces show the corresponding calculated IR spectra.

large magnification, whereas theory predicts an approximately 5:1 ratio of the S=O and CH$_2$ modes. The non-ergodic behavior outlined above provides a consistent explanation for the combined findings: As a result of incomplete IVR of the S=O modes, their excitation leads to a local "overheating" directly at the bridging linkage of the triple ion, which is then followed by dissociation of the noncovalent aggregate. In contrast, the energy of the photons absorbed by the *n*Bu$_4$N$^+$ groups dissipates in the numerous degrees of freedom of the ammonium ions, such that dissociation hardly occurs upon IRMPD.

One of several other explanations for the observed behavior (see the Supporting Information) would be that the bond strengths of the triple ions differ largely. However, the computed bond dissociation energies (BDEs) are all on the order of 100–120 kJ mol^{-1}. In addition to the BDEs, Table 1 includes the integrated areas of the bands arising from CH$_2$ bending and those of the X=O modes for triflate (X = S), acetate (X = C), and perchlorate (X = Cl). Comparison of the ratios predicted by theory with those from IRMPD further underscores the large discrimination of the CH$_2$ modes in case of [(Bu$_4$N$^+$)(TfO$^-$)(*n*Bu$_4$N$^+$)]. The effect is not general, however, in that the corresponding triple ion of acetate, [(Bu$_4$N$^+$)(AcO$^-$)(*n*Bu$_4$N$^+$)], which has a similar size and *m*/*z* value, behaves perfectly normally, that is ergodically. The perchlorate [(Bu$_4$N$^+$)(ClO$_4^-$)(*n*Bu$_4$N$^+$)] also shows some suppression of the CH$_2$ bending, but the effect is much less pronounced than for the triflate case.

Table 1: Ratios of the integrated areas[a] of the X=O stretching modes (ca. 1270 cm^{-1} for X = S, ca. 1590 cm^{-1} for X = C, and 1100 cm^{-1} for X = Cl) and the CH$_2$ modes at around 1490 cm^{-1} in the computed IR spectra and the experimental IRMPD data of several triple ions and their computed BDEs (in kJ mol^{-1}).

Species	Theory	Experiment	BDE
[(Me$_4$N$^+$)(TfO$^-$)(Me$_4$N$^+$)]	5:1	8:1	120
[(Me$_4$N$^+$)(TfO$^-$)(*n*Bu$_4$N$^+$)]	6:1	19:1	99[b] 124[c]
[(*n*Bu$_4$N$^+$)(TfO$^-$)(*n*Bu$_4$N$^+$)]	5:1	5000:1	103
[(*n*Bu$_4$N$^+$)(AcO$^-$)(*n*Bu$_4$N$^+$)][d]	3:1	3:1	90
[(*n*Bu$_4$N$^+$)(ClO$_4^-$)(*n*Bu$_4$N$^+$)][d]	6:1	38:1	101

[a] Integrations within ±50 cm^{-1} around the peak maxima in the respective spectra. From repetitions, the error of the experimental ratios is estimated as ±30%, which is also a reasonable figure for the computed IR data. [b] Formation of *n*Bu$_4$N$^+$. [c] Formation of Me$_4$N$^+$. [d] Spectra provided in the Supporting Information.

In conclusion, the data presented in Figure 1 and Figure 2 provide experimental evidence for incomplete IVR in noncovalent ion pairs of nitrogen-based cations. This effect appears to be particularly pronounced in the case of triflate as a counterion. The size dependence of the effect, derived from the comparison of the tetraalkylammonium ions, implies that the effect is due to a local "overheating" of the triflate moiety, rather than particularly efficient IVR of the anion. Such an "overheating" phenomenon can in turn be classified as a non-ergodic effect, which occurs in molecules of considerable size. Moreover, while the fragmentation of the triple ions only involves the cleavage of relatively weak, noncovalent bonds, the formation of triflic acid as a neutral product in the fragmentations of [*h*-**1**$^{2+}$·TfO$^-$] and [*s*-**1**$^{2+}$·TfO$^-$] indicates that the non-ergodic behavior occurs on a time scale, long enough to even include the formation of new chemical bonds.

In a more general perspective, the evidence for a non-ergodic behavior in noncovalent ion pairs may have implications far beyond IRMPD as a spectroscopic technique used in mass spectrometry. Thus, similar "overheating" phenomena have been suggested to explain the heartily debated specific microwave effects,[21] which often involve ion pairs.[22] While we are far from any conclusions in these directions, the effect as such is of broad interest and it will be exciting to probe other S=O anions for similar phenomena.

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