COLLISION-INDUCED SPECTRA: AN AVENUE TO INVESTIGATE MICROSCOPIC-SCALE DIFFUSION IN FLUIDS

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New data on the IR spectra induced by intermolecular interactions in liquid cryogenic mixtures at T=89 K (O$_2$ in LAr and LN$_2$ and binary O$_2$-Ar solutions in LN$_2$) are reported. The induced fundamental bands appear as diffuse pedestals (with FWHH$\approx$100 cm$^{-1}$) on which weak, paradoxically sharp lines (FWHH$\approx$2 cm$^{-1}$) develop at the 2326 and 1552 cm$^{-1}$ frequencies of the free-molecule vibrational transitions in N$_2$ and O$_2$, respectively. In LAr and LN$_2$ these lines were carefully separated and studied at varied O$_2$ concentrations up to $c=0.23$ mole fractions (mf). While the 1552 cm$^{-1}$ line scales as $c[O_2]^2$ and thus is induced by the O$_2$-O$_2$ interactions in a bulk of cryosolvent (Ar, N$_2$), the 2326 cm$^{-1}$ feature varies linearly with $c[O_2]$ and hence is caused by interaction of a guest (O$_2$) with a vibrating host (N$_2$). The impurity induction mechanism was further supported by our data on the binary O$_2$-Ar solutions in LN$_2$ recorded at the fixed $c[O_2]$ (0.03 and 0.06 mf) and the varied $c[Ar] \leq 0.2$ mf. Both series revealed the same (linear) enhancement of the sharp N$_2$ line by argon, in accord with our previous studies of the Ar-LN$_2$ system$^a$. The results suggest that the resonance 2326 cm$^{-1}$ feature is primarily due to the local distortion of the first coordination sphere around a vibrating N$_2$ by a guest molecule. We also notice that the resonance lines should be due to the dispersion- and overlap-induced dipole moments independent on the rotational degrees of freedom$^b$. As our previous studies of the H$_2$-LNe system showed$^c$, the unusual line sharpness is a conspicuous manifestation of the relative solvent-solute and solute-solute translations dramatically retarded in a liquid by a fast velocity relaxation, an effect directly related to the microscopic-scale diffusion. The collision-induced spectra thus open up new vistas for studies of microscopic liquid dynamics.

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