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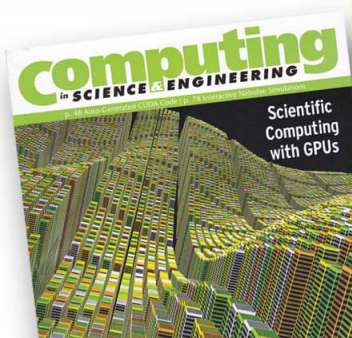
ERRATA

Erratum: "Molecular dynamics study of vibrational energy relaxation of CN⁻ in H₂O and D₂O solutions: An application of path integral influence functional theory to multiphonon processes" [J. Chem. Phys. 111, 5390 (1999)]

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A bug of the FORTRAN program has been found in the routine of kinetic energy matrix calculation with respect to Eulerian angles, which is used to obtain the transformation matrix from the adopted coordinates to the normal modes. This caused incorrect transition frequency of, mostly, rotational modes R and, hence, resulted in erroneous density of states $D(\omega)$ and spectral densities $\mathcal{J}(\omega)$. The corrected $D(\omega)$ and $\mathcal{J}_\beta(\omega)$, which play a central role in the theory, are presented in Figs. 1 and 4, respectively. With respect to $\mathcal{J}_\alpha(\omega)$, since no intensity was found at 2080 cm⁻¹ in the corrected spectrum, which is the same as before, it is not shown here. The change in the distribution in Figs. 1 and 4 are small, too. Thus, these corrections do not affect the most important conclusion that the relaxation is not caused by the single-phonon processes but the multi-phonon processes are all responsible for the relaxation.
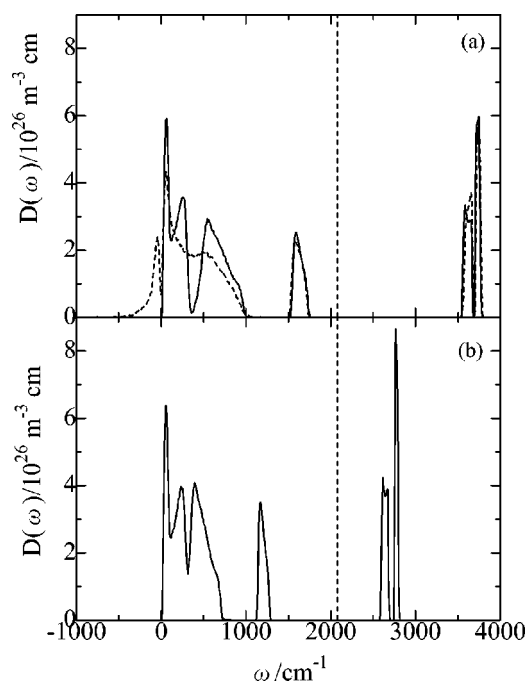
TABLE I. Relaxation time of the vibrationally first excited state of CN⁻.

System Solvation structure	CN⁻ in H₂O quenched	CN⁻ in H₂O instantaneous	CN⁻ in D₂O quenched
Present calculation	14 ps	7 ps	130 ps
Experiment[a]	28 ps	28 ps	71 ps

[a]Reference 13 in the original paper.

Quantitatively, calculated relaxation times changed to an extent, the correct values being listed in Table I. The values are, again, of the same order of magnitude as those measured experimentally. Further, isotope effect is reproduced well in the present case, too, between H₂O and D₂O solutions. In more detail, however, assignment of the contributing pairs of normal modes was erroneous. The corrected contributions are presented in Table II, which shows that the RB pair plays an important role in the relaxation in H₂O solution, while the RS pair is predominant in D₂O solution. Related discussions in the original paper should be read according to the tables here.

In spite of the corrections, effectiveness of the theory remains unchanged, presenting a promising tool for the quantum analysis of the vibrational relaxation. Finding of the bug is indebted to T. Mikami in our group.

FIG. 1. The density of states $D(\omega)$ of the solvent modes calculated for (a) the quenched (solid line) and the instantaneous (dashed line) H₂O solution and (b) the quenched D₂O solution. CN⁻ vibrational frequency $\tilde{\omega}_s$ is about 2080 cm⁻¹ (dotted line).

TABLE II. Contributions from various pairs of bath modes to the vibrational relaxation.

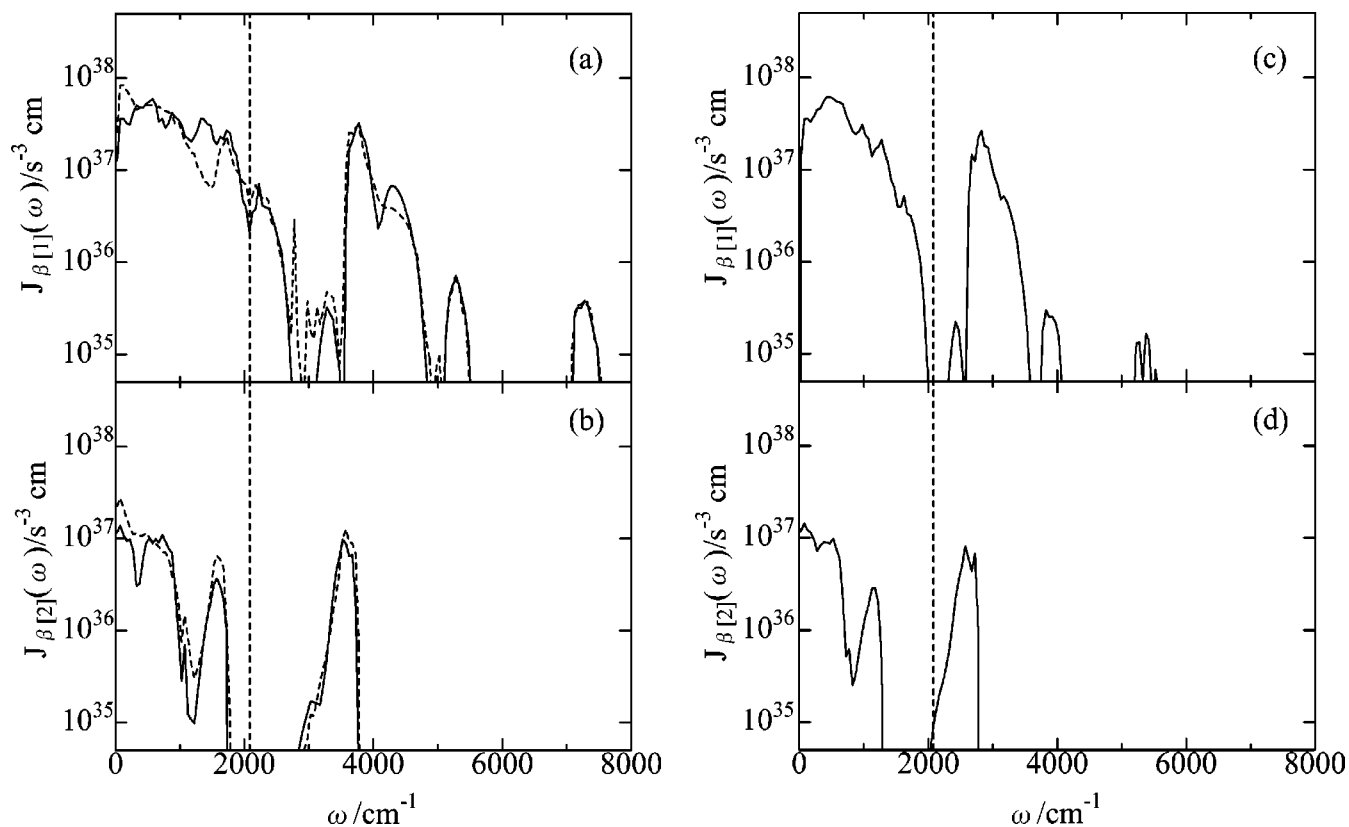| System Solvation structure	CN⁻ in H₂O quenched	CN⁻ in H₂O instantaneous	CN⁻ in D₂O quenched
TT	0 %	0 %	0 %
TR	0 %	0 %	0 %
TB	10 %	24 %	0 %
TS	0 %	0 %	1 %
RR	0 %	1 %	1 %
RB	90 %	75 %	2 %
RS	0 %	0 %	96 %
BB	0 %	0 %	0 %
BS	0 %	0 %	0 %
SS	0 %	0 %	0 %

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FIG. 4. Two-phonon spectral densities of $\mathcal{J}_{\beta[1]}(\omega)$, (a) and (c), and $\mathcal{J}_{\beta[2]}(\omega)$, (b) and (d), of sum- and difference-frequency modes, respectively. The solid lines in (a) and (b) represent the spectral density for the quenched H_2O solution and the dashed lines for the instantaneous H_2O solution. The solid lines in (c) and (d) are for the quenched D_2O solution. The dotted line at about 2080 cm^{-1} indicates the CN$^-$ vibrational frequency.