

### Details for MD simulation

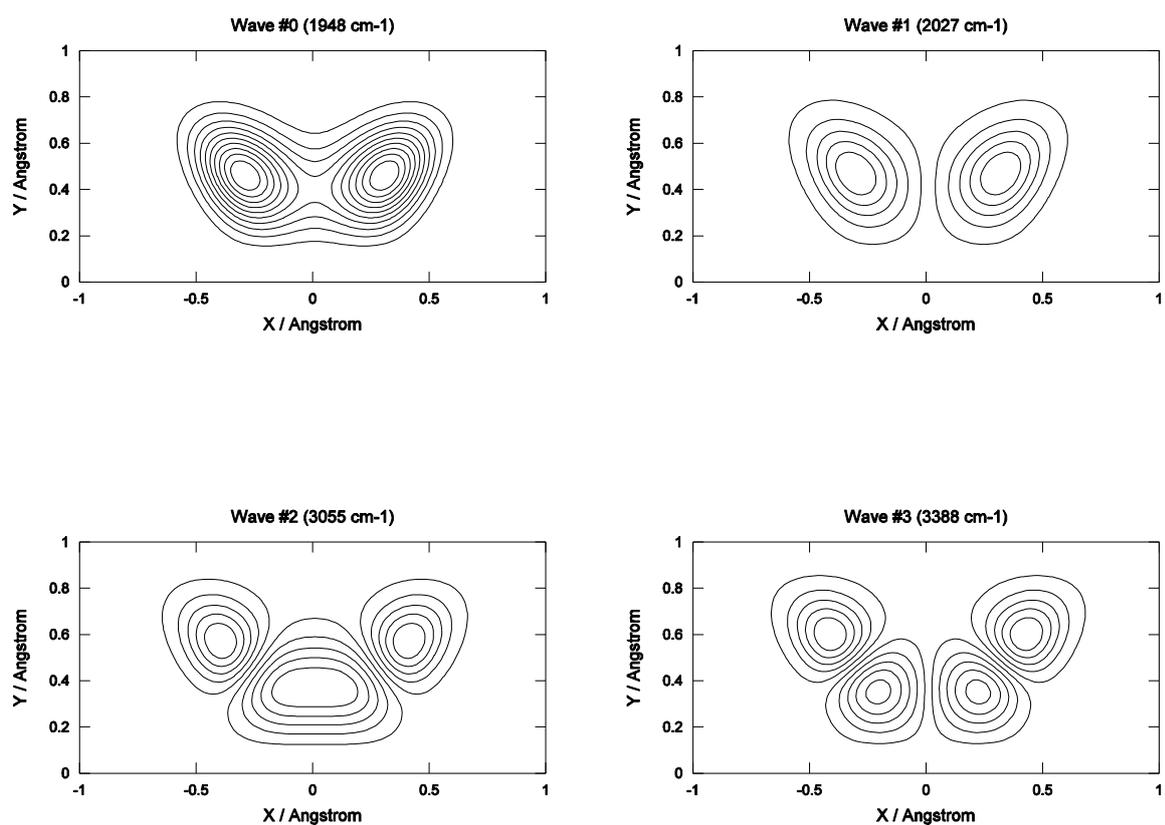
In order to generate an initial structure of the cluster model **2\_35H<sub>2</sub>O**, MD simulation was run for an NVT ensemble at 300 K with a time step of 1 fs and a cut-off distance of 12 Å using the AMBER11 package<sup>1</sup>. ESP charges and GAFF force field parameters<sup>2</sup> were used for the cation. A solvation sphere was generated with a radius of 20 Å from the center of solute, resulting in a simulation sphere containing one cation and 1012 TIP3P water molecules. During the MD runs, the cation was fixed and only water molecules were propagated. Two independent trajectories were run and the atom coordinates of the cation and closest solvent molecules were extracted from the snapshot at 2 ps for each run to obtain the initial structure of the cluster model.

The initial structure of cluster model **2Cl\_26MeCN** was also constructed from a snapshot of an MD trajectory. ESP charges and GAFF parameters were used for the cation and MeCN molecules. The simulation box contained one cation, one chloride ion and 520 MeCN molecules in a rectangular cell of 38.9 × 37.2 × 33.7 Å<sup>3</sup>. The cation was fixed and chloride ion and MeCN molecules were propagated with the SHAKE constrain. The periodic boundary condition was applied and the cut-off distance was set to 9 Å. From the snapshot at 2 ps, the atom coordinates of cation, chloride ion and 26 closest MeCN molecules were extracted to construct the initial structure of **2Cl\_26MeCN**. In the initial model thus obtained, the distance between the cation and Cl<sup>-</sup> was shorter than that obtained by the geometry optimization of the ion-pair with the CPCM method. The initial model was hence modified so that the position of Cl<sup>-</sup> relative to the cation was the same as the CPCM-optimized structure, and then the modified model was subjected to partial geometry optimization with the ONIOM (MP2/cc-pVDZ:PM3) method in which only the MeCN molecules were optimized. The optimized structure was used as the equilibrium point for the subsequent calculation for PES.

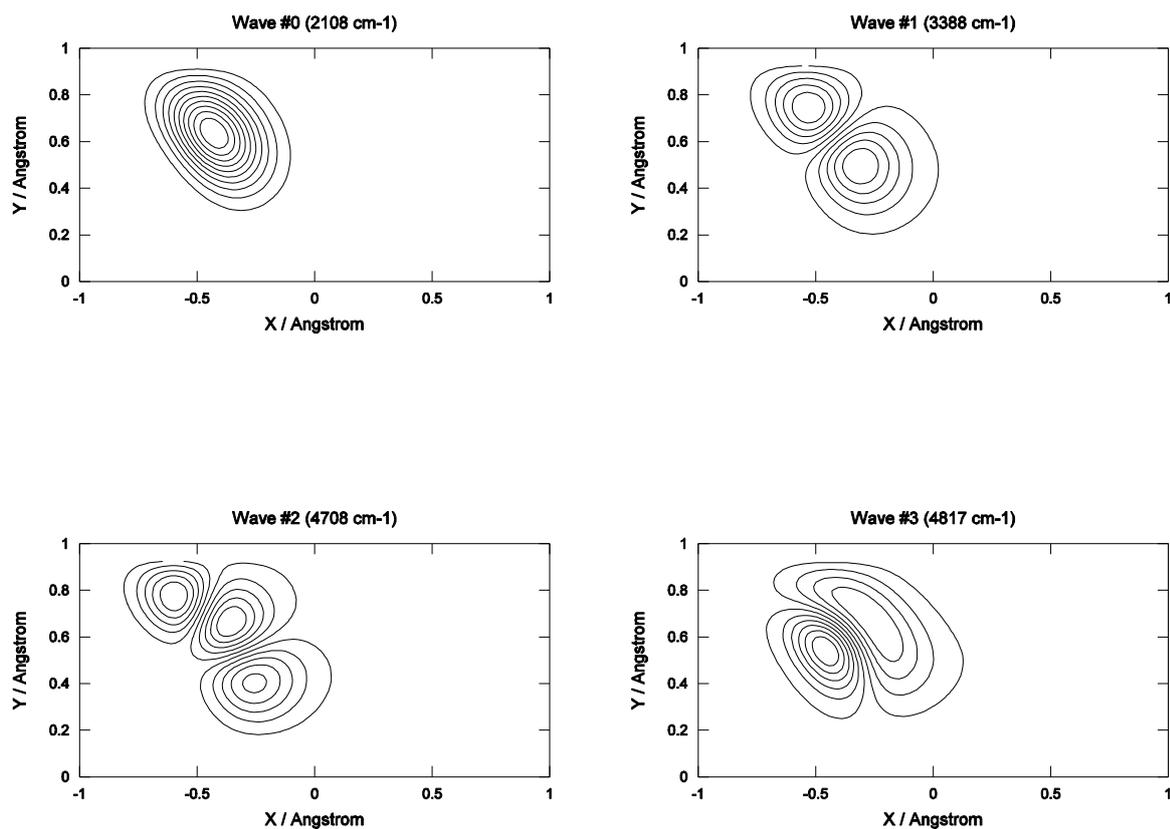
- 1 D. A. Pearlman, D. A. Case, J. W. Caldwell, W. S. Ross, T. E. Cheatman, III, S. DeBolt, D. Ferguson, G. Seibel and P. Kollman, *Comp. Phys. Commun.*, 1195, **91**, 1.
- 2 J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman and D. A. Case, *J. Comp. Chem.*, 2004, **25**, 1157.

### Complete description of reference 37

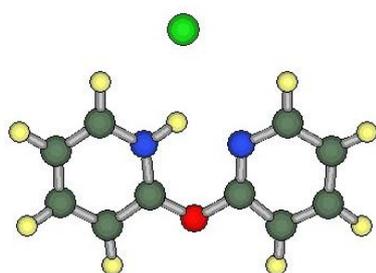
Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.



**Fig. S1** Wavefunctions for the lowest four states ( $\nu = 0, 1, 2$  and  $3$ ) of the in-plane motion of the bridging proton in **2** on the 2D PES shown in Fig. 7 (top). The abscissa and ordinate are the X- and Y-coordinates, respectively, of the proton. The contours are given from  $0.05\phi_{\max}$  to  $0.95\phi_{\max}$  for  $\nu = 0$  or from  $-0.45\phi_{\max}$  to  $0.45\phi_{\max}$  for the others. The positions of the nitrogen atoms are  $(\pm 1.283, 0, 0)$ . The minimum of the potential energy is located at  $(\pm 0.335, 0.467, 0)$ .



**Fig. S2** Wavefunctions for the lowest four states ( $\nu = 0, 1, 2$  and  $3$ ) of the in-plane motion of the bridging proton in  $2\text{Cl}_{26}\text{MeCN}$  on the 2D PES shown in Fig. 7 (bottom). The abscissa and ordinate are the  $X$ - and  $Y$ -coordinates, respectively, of the proton. The contours are given from  $0.05\phi_{\text{max}}$  to  $0.95\phi_{\text{max}}$  for  $\nu = 0$  or from  $-0.45\phi_{\text{max}}$  to  $0.45\phi_{\text{max}}$  for the others. The positions of N1, N1' and Cl are  $(-1.311, 0, 0)$ ,  $(1.311, 0, 0)$ , and  $(-0.266, 3.095, 0.026)$ , respectively. The minimum of the potential energy is located at  $(-0.442, 0.590, 0)$ .



**Fig. S3** Molecular structure of ion-pair  $2\text{Cl}$  optimized with the CPCM method (Solvent = MeCN). The chlorine atom is drawn in green.