MILLIMETERWAVE SPECTROSCOPY OF THE INTERNAL ROTATION BANDS OF Ne-DCN

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In 2005,[a] we reported the MMW specrtum of internal rotation bands (j=1-0 and 2-1) of Ne-HCN to analyzed the intermolecular potential energy surface (PES) between Ne and HCN, where j denotes the quantum number for the HCN internal rotation. In the present study, we have extended our observation to the Ne-DCN deuterated complex in the MMW region (78-175 GHz), and assigned the several DCN internal rotation bands such as the j=1-0 fundamental band (Σ_1-Σ_0 and Π_1-Σ_0) and the j=2-1 hot band (Σ_2-Σ_1, Π_2-Σ_1, Π_2-Π_1, and Δ_2-Π_1) for the ^{20}Ne-DCN and ^{22}Ne-DCN complexes. In total, 69 and 12 lines have been assigned to the ^{20}Ne-DCN and ^{22}Ne-DCN. The intermolecular stretch band between Ne and DCN, however, was not observed in this frequency region. Analysis shows that the Σ_1 and Π_1 sublevels for j=1 state are located at 134 and 105 GHz, respectively, above the j=0 ground state (Σ_0), while the Σ_2, Π_2, and Δ_2 sublevels of j=2 state are located at 286, 276, and 257 GHz with different order from that for the normal species.

The observed MMW frequencies for Ne-DCN were analyzed with two dimensional ($\theta - R$) PES freezing the freedom in DCN moiety. The PES given by CCSD(T) level $ab\ initio$ calculation[b] was modified by adding sixteen extra parameters and fitted to the observed frequencies of internal rotation bands of both ^{20}Ne and ^{22}Ne species. The ($\theta - R$) PES thus fitted has a global minimum in the linear configuration (Ne$\cdots$D–C–N) with a well depth of 64.1 cm^{-1}, and a saddle point located in the anti-linear configuration (D–C–N$\cdots$Ne) by 18.4 cm^{-1} higher than the global minimum. The j=0 ground vibrational state is located by 4.8 cm^{-1} higher than the saddle point. The PES is anisotropic because the center-of-mass distance between Ne and DCN changes much along the minimum energy path, 4.230, 3.477, and 4.020 Å in the linear, T-shaped, and anti-linear forms, together with their energies. The PES estimated for Ne-DCN is very similar to that of Ne-HCN, but the global minimum is by 1.1 cm^{-1} deeper than that of Ne-HCN, due to the frozen model of the HCN/DCN moiety and also our observation is quite limited to the bottom of PES, e.g. highest observed state (Σ_2) is still 30 cm^{-1} below the dissociation limit.

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[a] K. Harada, K. Tanaka, and S. Nanbu, *The 60th International Symposium on Molecular Spectroscopy*, **RH01**, (2005).

[b] R. R. Toczylowski, F. Doloresco, and S. M. Cybulski, *J. Chem. Phys.* **114**, 851 (2001).