

## MILLIMETERWAVE SPECTROSCOPY OF THE INTERNAL ROTATION BANDS OF Ne-DCN

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In 2005,<sup>a</sup> we reported the MMW spectrum of internal rotation bands ( $j=1-0$  and  $2-1$ ) of Ne-HCN to analyze 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 ( $\Sigma_1-\Sigma_0$  and  $\Pi_1-\Sigma_0$ ) and the  $j=2-1$  hot band ( $\Sigma_2-\Sigma_1$ ,  $\Pi_2-\Sigma_1$ ,  $\Pi_2-\Pi_1$ , and  $\Delta_2-\Pi_1$ ) for the  $^{20}\text{Ne-DCN}$  and  $^{22}\text{Ne-DCN}$  complexes. In total, 69 and 12 lines have been assigned to the  $^{20}\text{Ne-DCN}$  and  $^{22}\text{Ne-DCN}$ . The intermolecular stretch band between Ne and DCN, however, was not observed in this frequency region. Analysis shows that the  $\Sigma_1$  and  $\Pi_1$  sublevels for  $j=1$  state are located at 134 and 105 GHz, respectively, above the  $j=0$  ground state ( $\Sigma_0$ ), while the  $\Sigma_2$ ,  $\Pi_2$ , and  $\Delta_2$  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<sup>b</sup> was modified by adding sixteen extra parameters and fitted to the observed frequencies of internal rotation bands of both  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  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  $64.1\text{ cm}^{-1}$ , and a saddle point located in the anti-linear configuration (D-C-N $\cdots$ Ne) by  $18.4\text{ cm}^{-1}$  higher than the global minimum. The  $j=0$  ground vibrational state is located by  $4.8\text{ cm}^{-1}$  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  $1.1\text{ cm}^{-1}$  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 ( $\Sigma_2$ ) is still  $30\text{ cm}^{-1}$  below the dissociation limit.

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<sup>a</sup>K. Harada, K. Tanaka, and S. Nanbu, *The 60th International Symposium on Molecular Spectroscopy*, **RH01**, (2005).

<sup>b</sup>R. R. Toczyłowski, F. Doloresco, and S. M. Cybulski, *J. Chem. Phys.* **114**, 851 (2001).