

**Millimeter-wave spectroscopy of He-HCN and He-DCN:
Energy levels near the dissociation limit.
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The He-HCN complex is a weakly bound complex. We have observed the the $j=1-0$ and $2-1$ internal rotation and intermolecular stretching bands of He-HCN and He-DCN by millimeter-wave absorption spectroscopy. The upper state of several observed transitions were found to be located above the "dissociation limit" (D_0). These levels are bound due to the parity conservation. The potential energy surface (PES) fitted to the observed transitions has a global minimum in the linear He--HCN configuration with a depth of 29.9 cm^{-1} and has a saddle point at the anti-linear He--NCH configuration. Life times of several quasi-bound levels are predicted for both isotopic species.

The He-HCN complex is a weakly bound complex with binding energy of about 9 cm^{-1} . We have observed the internal rotation band ($j = 1 \leftarrow 0$) of the He-HCN complex by millimeter-wave absorption spectroscopy combined with a pulsed-jet expansion technique and reported the potential energy surface (PES) to reproduce the observed transition frequencies.¹

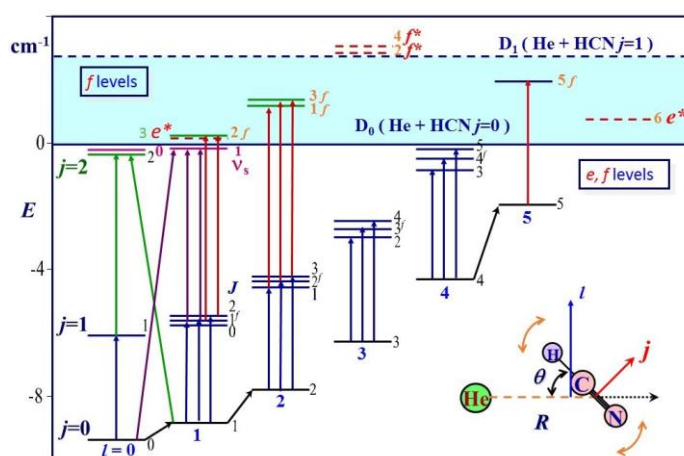


Fig. 1. Energy levels and observed transitions of He-HCN

The measurement was extended to the internal rotation hot band (the $j=2-1$ band) and the intermolecular stretching band (ν_s). The vdW bands of He-DCN were also observed.

[Energy levels and observed transitions]

The energy levels and observed transitions of He-HCN are illustrated in Fig. 1. The j , l , J are the internal rotation angular momentum of HCN, the angular momentum for the end-over-end rotation of He-HCN, and the total angular momentum of the complex. The intermolecular stretching first excited state (ν_s) and the internal rotation second excited state ($j = 2$) are determined to be located at 9.140 and 9.053 cm^{-1} above the ground state, very close to the dissociation limit (D_0) of 9.316 cm^{-1} .

The several transitions to the bound states above the "dissociation limit" (D_0) have been observed for He-HCN. The level of He-HCN has the $+/-$ parity if $j + l$ is even/odd and it is also labeled as e/f when $J - j - l$ is even/odd. Since the parity and the total angular momentum J are conserved, the e/f label is conserved even in the dissociation process. If the He-HCN complex dissociates to He and HCN with the $j=0$ rotational ground state, the He + HCN system has the e symmetry, because $J = l$. On the other hand, when the complex dissociates to He and HCN with the $j=1$ rotational excited state, the system splits into three components; two e ($J = l \pm 1$) and one f ($J = l$) state. Due to the conservation of e/f -symmetry, the f -levels of the He-HCN complex dissociate to He + HCN ($j=1$) because it contains

the lowest f -level. The f -levels have the other dissociation limit of D_1 , located by 2.96 cm^{-1} higher than the dissociation limit D_0 for the e levels. The present analysis indicates that four and three f levels are bound for He-HCN and He-DCN above the "dissociation limit" (D_0).

In the analysis, we also predicted the quasi-bound energy levels by the method of Hazi and Taylor.²⁾ The four and three levels (both of e and f labels) are predicted to be quasi-bound for He-HCN and He-DCN. These levels have finite life times as listed in Table 1 since the centrifugal barriers V_{\max} are higher than the energies of these levels.

Table 1. Metastable States of He-HCN

j	l	J	$E(\text{cm}^{-1})$	$V_{\max}(0^\circ)$	$\tau(\text{ns})$
He-HCN					
0	6	6 ^e	0.7509	2.848	1.8
2	1	3 ^e	0.32	0.453	0.021
2	3	2 ^f	3.0168	3.118	14
2	3	4 ^f	3.2538	3.918	16
He-DCN					
0	6	6 ^e	0.2084	2.849	470
2	3	5 ^e	1.431	1.752	0.26
2	4	5 ^f	3.73	4.168	0.053

[Potential energy surface]

The PES fitted to reproduce the observed transition frequencies of He-HCN has a global minimum in the linear He—HCN configuration with a depth of 29.812 cm^{-1} and has a saddle point at the anti-linear He--NCH configuration with a depth of 20.812 cm^{-1} . The potential height on the minimum energy path (MEP) of the PES have been illustrated in Fig. 2. The PES of He-HCN obtained in the analysis is similar to the theoretical PES,³⁾ although the present PES has by 1 cm^{-1} smaller potential anisotropy ($V_{\text{MEP}}(\theta=\pi) - V_{\text{MEP}}(\theta=0)$) than the theoretical one.

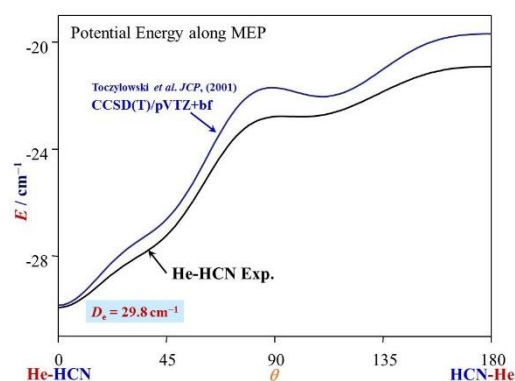


Fig. 2. Potential height on MEP

[Long range potential parameters]

In the present analysis, we have used a coupled potential of a exponential ($e^{-\beta R}$) repulsive potential and a asymptotic long range attractive potential. In total, 8 short range and 8 long range potential parameters have been determined. The long range potential parameters obtained are compared in Table 2. The C_{nl} is the coefficient of the $P_l(\cos\theta) \cdot R^{-n}$ dependence term. The PES reported by CCSD(T)/cc-pVTZ *abinitio* calculation³⁾ was also fitted by the same potential function and parameters obtained are also compared in Table 2. The long range potential parameters obtained for the normal and deuterated species are similar and also consistent to the parameters fitted to the theoretical PES.

Table 2. Long Range Parameters of He-HCN and He-DCN in au.

	He-HCN	He-DCN	CCSD(T)/cc-pVTZ
C_{60}	16.353(60)	16.924(42)	16.24(15)
C_{80}	280.0(40)	230.4(29)	234.(13)
C_{71}	28.593(98)	29.124(130)	23.8(28)
C_{91}	906.3(134)	822.0(86)	950.(220)
C_{62}	4.480(123)	5.673(96)	5.56(26)
C_{82}	484.2(86)	379.9(75)	332.(22)
C_{73}	26.19(30)	27.244(77)	11.0(24)
C_{93}	---	---	1130.(160)
C_{84}	118.01(52)	115.17(114)	70.2(43)

¹J. Chem. Phys. **117**, 7041(2002).

²Phys. Rev. A1, 1109 (1970).

³J. Chem. Phys. 114, 851 (2001).