



Fourier-transform microwave spectroscopy of the H₂–HCN complex

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ABSTRACT

Fourier-transform microwave spectroscopy was applied to observe the $J = 1-0$ rotational transition of the H₂–HCN complex for both the *ortho*- and *para*-H₂ species to obtain improved molecular constants by an analysis combined with the millimeter-wave data. It was confirmed that the *para*- and *ortho*-H₂ species have different configurations: namely H₂ is attached to the H end of HCN in the former, while to the N end in the latter. For the *ortho*-H₂ species, the hyperfine splitting due to the magnetic interaction between the hydrogen nuclei was observed to give the nuclear spin–spin coupling constant $d_{\text{H}} = 54.6(38)$ kHz.

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1. Introduction

In our previous paper [1], we have reported the pure rotational spectrum of the H₂–HCN complex observed by millimeter-wave (MMW) spectroscopy in the frequency range of 68–148 GHz. Four pure rotational lines, split into hyperfine components, were observed in the range from $J = 3-2$ to $6-5$ for both the *para*- and *ortho*-H₂–HCN. The ground state of (*o*)H₂–HCN, as well as that of (*p*)H₂–HCN, was confirmed to have the Σ symmetry because the observed spectrum did not show further splitting expected for the Π symmetry. From the observed rotational constants, the average distance between the centers of mass of H₂ and HCN was derived to be 3.9613(35) and 4.229(11) Å, respectively, for (*o*)H₂– and (*p*)H₂–HCN, suggesting totally different configurations in (*o*)H₂– and (*p*)H₂–HCN: namely for the *para*-H₂ species, H₂ is attached to the H end of HCN, while for the *ortho*-H₂ species to the N end. This conclusion from the MMW study is consistent with the infrared spectrum observed in helium droplets [2,3], where the red shift of the CH stretching frequency for (*o*)H₂–HCN (0.286 cm^{-1}) is smaller by an order of magnitude than that for (*p*)H₂–HCN (2.143 cm^{-1}). The drastic difference in the red shift is caused by the different configurations in the *ortho*- and *para*-H₂ species, because the CH-stretching frequency is less affected when H₂ is attached to the N end than to the H end.

In the present paper, we have extended the observation to the $J = 1-0$ rotational transition for both (*o*)H₂– and (*p*)H₂–HCN by Fou-

rier-transform microwave (FTMW) spectroscopy. The extremely high resolution of the FTMW spectrometer gives us information on the nuclear spin interaction of the H₂ part, as well as that of the HCN part.

The spectroscopic detection of the hydrogen-molecule containing complexes has been reported mostly in the infrared region for H₂–H₂ [4], H₂–Ar [5], H₂–Kr [5], H₂–HF [6–9], H₂–HCl [10], H₂–CO [11–13], H₂–CH₄ [14], H₂–H₂O [15], and H₂–HCN [1–3]. Lightness of the H₂ containing complexes has hampered the observation of rotational spectra. The H₂–CO complex is an exceptional case for which *b*-type rotational transitions connecting different K_a stacks were detected in the millimeter-wave (MMW) region [12]. Recently we have observed pure rotational spectra of H₂–H₂O [16] and H₂–HCl [17] in the MMW region.

2. Experimental

A Balle-Flygare-type FTMW spectrometer at the University of Tokyo with the frequency coverage from 4 to 40 GHz was used. Details of the apparatus have been reported previously [18,19]. The gas mixture of H₂ (~25%) and He (~75%) seeded with 0.5% HCN was injected into the cell through a pulsed valve with a 0.8 mm orifice (General Valve). The operating pressure inside the cell was 0.01 mTorr when the stagnation pressure was 9–10 atm and the repetition rate of the pulsed valve was 5 Hz. The generated complexes were rotationally cooled in a supersonic expansion to a few K. The microwave cavity frequency was swept in steps of 1 MHz, and free induction decay signals for typically 100–1000 jet pulses were averaged. The overall accuracy in observed line frequencies is estimated to be a few kHz. The jet pulse was introduced in the absorption cell either parallel or perpendicular to the cavity axis. When Ne was used as buffer gas instead of He, spectral lines of (*o*)H₂–HCN were observed, but lines of (*p*)H₂–HCN disappeared.

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3. Observed spectrum and analysis

The rovibrational levels of H₂–HCN are complicated due to the two extremely floppy internal rotors (H₂ and HCN) in the complex. The total angular momentum except for nuclear spins is given by $\mathbf{J} = \mathbf{j}_{\text{HCN}} + \mathbf{j}_{\text{H}_2} + \mathbf{l}$, where \mathbf{l} denotes the angular momentum for the end-over-end rotation of the whole complex and \mathbf{j}_{HCN} and \mathbf{j}_{H_2} are respectively angular momenta for internal rotation of HCN and H₂. Projections of \mathbf{J} , \mathbf{j}_{HCN} and \mathbf{j}_{H_2} onto the axis connecting the center of mass of HCN and that of H₂ (hereafter called the intermolecular axis) are denoted by k , k_{HCN} and k_{H_2} , where we have $k = k_{\text{HCN}} + k_{\text{H}_2}$, because \mathbf{l} is perpendicular to the intermolecular axis. \mathbf{j}_{HCN} as well as k_{HCN} vanishes in the ground state. Thus we have the Σ_0 ground state for the *para*-H₂ species with $j_{\text{H}_2} = 0$, while for the *ortho*-H₂ species with $j_{\text{H}_2} = 1$, the ground state could be either Σ_0 or Π_0 state, depending on the anisotropy of the potential. The actual ground state for the *ortho*-H₂ species is of Σ_0 symmetry.

Guided by a prediction from the MMW study [1], the $J = 1-0$ transition of (o)H₂–HCN was searched, and observed at 25768 MHz by 17 MHz higher than the prediction. The observed spectrum shown in Figure 1 is split into three hyperfine components due to the quadrupole interaction of the N nucleus, $F_1 = 1-1$, 2-1, and 0-1, and each component, except for $F_1 = 0-1$, is split further into three components due to the nuclear spin–spin interaction of the H nuclei ($I_{\text{H}_2} = 1$), where F_1 and F are for the angular momenta $\mathbf{F}_1 = \mathbf{J} + \mathbf{I}_N$ and $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}_{\text{H}_2}$, respectively. Signals for (o)H₂–HCN were rather strong and even the weaker $F_1 = 0-1$ component ($\Delta F_1 = -\Delta J$) was observed with good signal to noise ratio as shown in Figure 1. They were observed with Ne as well as He buffer gas. The line width of the hyperfine components was 28 kHz FWHM, corresponding to the Doppler width in the jet expansion with He as the carrier gas.

On the other hand, for the $J = 1-0$ transition of (*p*)H₂–HCN, no signal was found with Ne buffer gas in spite of the careful search in the frequency region of 23.2–23.7 GHz predicted from the MMW study [1]. But when the buffer gas was changed to He, weak lines were recorded at 23665 MHz after accumulation of 1000 times: the line position was by 182 MHz higher than the prediction from the MMW results. The observed spectrum shown in Figure 2 is assigned to the $J = 1-0$ transition of (*p*)H₂–HCN, split by the quadrupole interaction of the nitrogen nucleus ($I_N = 1$) into three

hyperfine components, $F = 1-1$, 2-1, and 0-1, where F corresponds to the total angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{I}_N$. The line intensity was rather weak, less than one sixth that for (o)H₂–HCN, and the weaker $F = 0-1$ component ($\Delta F = -\Delta J$) was 1.5 times of the noise level.

In total three and seven hyperfine components of the $J = 1-0$ rotational transition were identified for the Σ_0 ground state of (*p*)H₂– and (o)H₂–HCN, respectively, as listed in Table 1. The rotational energy E_r in the Σ_0 ground state including centrifugal distortion terms is given by,

$$E_r = B_0 f - D_0 f^2 + H_0 f^3 + L_0 f^4 + M_0 f^5, \quad (1)$$

where f denotes $J(J+1)$. Coriolis interaction between the Σ_0 and Π_0 substates is neglected because the Σ_0 and Π_0 sublevels are separated by several tens of cm^{-1} [3].

The quadrupole hyperfine interaction due to the N nucleus ($I_N = 1$) is given by,

$$H_{eqQ} = (1/4)(eqQ_0 + eqQ_D \mathbf{J}^2 + eqQ_H \mathbf{J}^4)(3I_{Nz}^2 - \mathbf{I}_N^2), \quad (2)$$

where \mathbf{I}_N represents the nuclear spin of N and the centrifugal distortion effect was taken into account by expressing the coupling constant as a power series in \mathbf{J}^2 . We also include the nuclear spin-rotation interaction of N,

$$H_{srN} = -c_N \mathbf{I}_N \cdot \mathbf{J}, \quad (3)$$

where c_N is the nuclear spin-rotation coupling constant.

The hyperfine interaction of the H₂ part (for *ortho*-H₂ species) originates from two sources, $H_{srH} = H_{srH} + H_{ssH}$ [20,21]. The first term H_{srH} denotes the interaction between H nuclear spins and H₂ internal rotation,

$$H_{srH} = -c_H \mathbf{I}_{\text{H}_2} \cdot \mathbf{j}_{\text{H}_2}, \quad (4)$$

where \mathbf{I}_{H_2} is the resultant nuclear spin of H₂ and c_H is the nuclear spin-rotation interaction constant. The second term H_{ssH} denotes the nuclear spin–spin interaction,

$$H_{ssH} = [5d_H/(2j_{\text{H}_2} - 1)(2j_{\text{H}_2} + 3)] [3(\mathbf{I}_{\text{H}_2} \cdot \mathbf{j}_{\text{H}_2})^2 + (3/2)\mathbf{I}_{\text{H}_2} \cdot \mathbf{j}_{\text{H}_2} - I_{\text{H}_2}^2 j_{\text{H}_2}^2], \quad (5)$$

where d_H is the nuclear spin–spin interaction constant for the H₂ moiety. For the *para*-H₂ species, the nuclear magnetic interactions in Eqs. (4), (5) vanish because both I_{H_2} and j_{H_2} are zero. The energy matrix of the effective Hamiltonian was constructed using the case- $(b)_\beta$ base functions, $|J, k, I_N, F_1, I_{\text{H}_2}, F, M_F\rangle$.

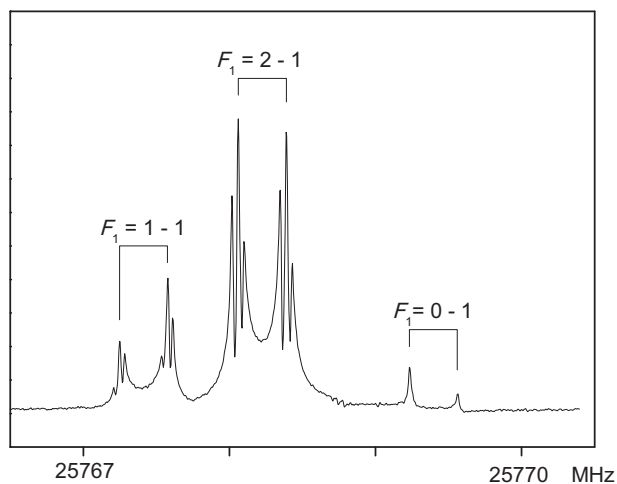


Figure 1. The $J = 1-0$ rotational transition of *ortho*-H₂–HCN in the Σ_0 ground state. The spectrum is split into three components, $F_1 = 1-1$, 2-1, and 0-1, due to the nitrogen nuclear quadrupole interaction. The two components, $F_1 = 1-1$ and 2-1, are further split into three components, due to the nuclear spin–spin interaction of the H₂ part.

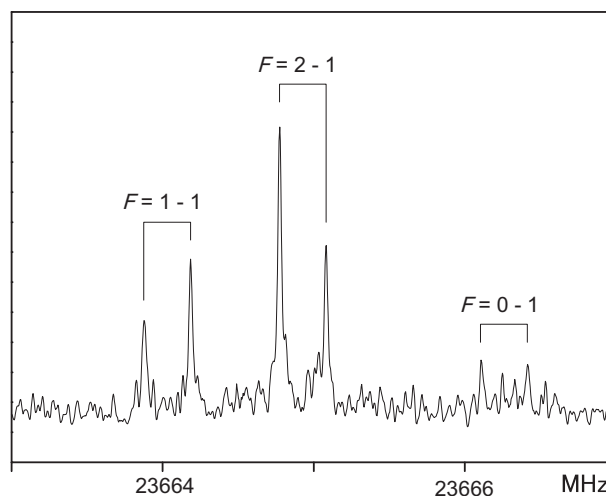


Figure 2. The $J = 1-0$ rotational transition of *para*-H₂–HCN in the Σ_0 ground state. The spectrum is split into three components, $F = 1-1$, 2-1, and 0-1, due to the nitrogen nuclear quadrupole interaction.

Table 1
Observed rotational transition frequencies of $J = 1-0$.

| Species | $F'_1 - F''_1$ | $F' - F''$ | Observed ^a | O-C ^b |
|-----------------------------------|----------------|------------|-----------------------|------------------|
| <i>para</i> -H ₂ -HCN | | 1-1 | 23664.0327 | -1.2 |
| | | 2-1 | 23664.9289 | 1.9 |
| | | 0-1 | 23666.2638 | 2.9 |
| <i>ortho</i> -H ₂ -HCN | 1-1 | 0-1 | 25767.3725 | 4.3 |
| | | 2-2, 1 | 25767.4150 | -2.3 |
| | | 1-2, 1, 0 | 25767.4486 | -1.5 |
| | 2-1 | 2-2, 1 | 25768.1818 | -1.1 |
| | | 3-2 | 25768.2254 | -6.6 |
| | | 1-2, 1, 0 | 25768.2669 | 7.6 |
| | 0-1 | 1-2, 1, 0 | 25769.3989 | -0.2 |

^a In MHz.^b Observed minus calculated frequency in kHz.

The observed rotational transitions summarized in Table 1 were analyzed to obtain the molecular constants in the Σ_0 ground state. The MMW line frequencies reported in Ref. [1] (8 and 10 hyperfine components of the four rotational transitions, respectively, for the *para*-H₂ and *ortho*-H₂ species) were also included in the fitting, given one hundred times less weights than the present FTMW lines. The rotational constant B_0 and four centrifugal distortion constants, D_0 , H_0 , L_0 , and M_0 , were adjusted to fit the observed spectrum, although five rotational lines were observed, together with the quadrupole hyperfine interaction constants. For the *ortho*-H₂ species, the nuclear spin-spin coupling constant d_H for the H nuclei was added as an adjustable parameter. The derived molecular constants are summarized in Table 2 with uncertainties in parentheses corresponding to one standard deviation. The residual of the fit was less than 8 kHz consistent with the observed linewidth of about 28 kHz.

4. Discussion

The rotational constant obtained for (*p*)H₂-HCN, 11 887.3394 (30) MHz, and that for (*o*)H₂-HCN, 12 910.5780(18) MHz, are by 116.786 MHz and 10.870 MHz, respectively, larger than our previous MMW values [1], indicating limited validity of the power series expansion of the rotational energy in f [Eq. (1)], especially for the *para*-H₂ species, because of the extreme floppiness of the complex. The rotational constant for (*p*)H₂-HCN is smaller by 1023.239 MHz (8.61%) than that of (*o*)H₂-HCN, reflecting drastic difference in structure between *ortho*- and *para*-H₂ species, as discussed in Ref. [1].

The centrifugal distortion constants $D_0 = 13.59511(68)$ and 29.1210(14) MHz, respectively, for (*o*)H₂- and (*p*)H₂-HCN are extremely large, and three more higher order centrifugal distortion constants (H_0 , L_0 and M_0) were employed to reproduce the observed line frequencies. The D_0 value for the *para*-H₂ species is lar-

Table 2
Molecular constants of H₂-HCN.^a

| Constant | <i>para</i> -H ₂ -HCN ^b | <i>ortho</i> -H ₂ -HCN ^b | Unit |
|----------|---|--|------|
| B_0 | 11887.3394 (30) | 12910.5780(18) | MHz |
| D_0 | 29.1210(14) | 13.59511(68) | MHz |
| H_0 | 860.07(11) | 168.313(59) | kHz |
| L_0 | -18.9350(35) | -2.2924(19) | kHz |
| M_0 | 180.196(36) | 16.769(20) | Hz |
| eqQ_0 | -3.058(26) | -2.6053(100) | MHz |
| eqQ_D | -44.1(115) | -17.06(164) | kHz |
| eqQ_H | -1.91(49) | - | kHz |
| c_N | - | 3.3(16) | kHz |
| d_H | - | 54.6(38) | kHz |

^a In parentheses are 1σ uncertainties in units of the last digit. MMW lines in Ref. [1] were also included in the analysis.^b Σ_0 ground state.

ger (2.14 times) than that of the *ortho*-H₂ species, and it is also the case for H_0 (860.07(11) and 168.313(59) kHz, respectively), suggesting much smaller binding energy for the *para*-H₂ species than for the *ortho*-H₂ species. The force constant for the vdW stretching vibration derived from the D_0 value is $k_s = 0.2837 \mu\text{dyne}/\text{\AA}$ for the *para*-H₂ species, about one third that of the *ortho*-species, 0.7785 $\mu\text{dyne}/\text{\AA}$. The force constant for (*o*)H₂-HCN is smaller than that of Ar-HCN ($k_s = 1.023 \mu\text{dyne}/\text{\AA}$) [22], but larger than that of Ne-HCN ($k_s = 0.5018 \mu\text{dyne}/\text{\AA}$) [23], while the force constant for (*p*)H₂-HCN is as small as that for He-HCN ($k_s = 0.2349 \mu\text{dyne}/\text{\AA}$) [24]. The vdW stretching frequencies are calculated to be 16.023 and 26.542 cm^{-1} for (*p*)H₂- and (*o*)H₂-HCN, respectively.

The determined nuclear quadrupole coupling constant for (*p*)H₂-HCN, -3.058(26) MHz, is larger than the previous MMW result, -2.22(17) MHz [1], although that for (*o*)H₂-HCN, $eqQ_0 = -2.6053(100)$ MHz, is almost the same as the previous value, -2.653(63) MHz. The molecular constants for (*p*)H₂-HCN, eqQ_0 as well as B_0 , changed conspicuously when the present FTMW data for the $J = 1-0$ transition were included in the analysis, indicating their strong J -dependence. The centrifugal distortion correction constant eqQ_D for (*o*)H₂-HCN, -17.06(164) kHz, is comparable to that of Ne-HCN, -12.7 kHz [23], but the eqQ_D constant for (*p*)H₂-HCN, -44.1(115) kHz, is much larger. Moreover, a higher order constant, $eqQ_H = -1.91(49)$ kHz, is needed for the *para*-H₂ species.

From the quadrupole coupling constants, the average values of $\langle P_2(\cos\theta) \rangle$, where θ is the angle between the HCN moiety and intermolecular axis, is calculated employing the relation $eqQ_0 = ! eqQ_{\text{HCN}} \langle P_2(\cos\theta) \rangle$, where eqQ_{HCN} is the quadrupole coupling constant for the free HCN molecule, -4.7091(1) MHz [25]. Then the mean amplitudes of θ , defined as $\arccos(\langle (\cos\theta)^2 \rangle^{1/2})$, are derived to be 33.075(89)° and 28.91(25)° for the *ortho*- and *para*-H₂ species, respectively: their previous values are 32.65(46)° and 36.4(22)° [1] and the large change in the value of *para*-H₂ species may be due to the large J -dependence in eqQ . The mean amplitudes are comparable to that of Ar-HCN, 30.97° [22], but much smaller than those of Ne-HCN, 46.8° [23], and He-HCN, 51.5° [26], implying the H₂ molecule hinders the internal rotation of HCN much more than the Ne and He atoms.

It is interesting to note that the mean amplitude of θ is smaller by 4.2° for (*p*)H₂-HCN than for (*o*)H₂-HCN, although the amplitude of the vdW stretching vibration is much larger for the former than for the latter, as supposed from the stretching force constants of (*p*)H₂-HCN which is about one third that of (*o*)H₂-HCN. This may suggest that the effective two dimensional potential energy surface (PES) $V(R, \theta)$, where R denotes the distance between the centers of mass of H₂ and HCN, has quite different forms in *para*- and *ortho*-H₂ species. The PES for (*o*)H₂-HCN has a shallower valley along the minimum energy path (MEP) than that for (*p*)H₂-HCN. The different shapes of PES are conceivable, if the *para*- and *ortho*-H₂ species have different configurations, where H₂ is faced to the H and N ends, respectively, of HCN. It is interesting to observe the HCN internal rotation bands ($j_{\text{HCN}} = 1-0$) of (*p*)H₂-HCN to obtain the internal rotation band frequency, and to discuss in comparison with those of (*o*)H₂-HCN, which we have already reported [27].

The nuclear spin-spin coupling constant determined for the *ortho*-H₂ species, $d_H = 54.6(38)$ kHz, agrees with that for the free H₂ molecule, $d_H = 57.670(27)$ kHz, determined by molecular beam experiments [28,29]. The coupling constant is given by $d_H = (4/5) (\mu_H)^2 \langle r^{-3} \rangle$, where μ_H is the magnetic dipole moment of a proton and r is the distance between the two protons. The present result is consistent with the assumption that the H₂ bond length remains unchanged on complexation with HCN.

The nuclear spin-rotation coupling constant c_H in Eq. (4) was not determined in the present analysis, although the *ortho*-H₂ species has non-zero angular momentum of $j_{\text{H}_2} = 1$: note that the c_H

constant of the free H₂ molecule is 113.846(85) kHz [28,29]. This is accounted for as follows. The component of \mathbf{j}_{H_2} parallel to the intermolecular axis has no matrix element within the Σ_0 ground state of (*o*)H₂-HCN, where k_{H_2} equals to zero. The perpendicular component of \mathbf{j}_{H_2} has matrix elements connecting the Σ_0 and Π_0 substates, but they give virtually zero contribution, because the Π_0 substate is separated from the Σ_0 ground state by several tens of cm^{-1} .

The spin-rotation coupling constant of the N nucleus, $c_{\text{N}} = 3.3(16)$ kHz, is about one third that for the HCN molecule, $c_{\text{N}} = 10.4(3)$ kHz [25]: the observed value is consistent with that of HCN when they are normalized by rotational constants as c_{N}/B_0 , because the rotational constant B_0 of HCN is about 3.4 times that for (*o*)H₂-HCN.

The average distances $\langle R \rangle$ between the centers of mass of H₂ and HCN subunits are calculated to be 3.9617(5) and 4.1589(13) Å for the *ortho*- and *para*-H₂ species, respectively, from the derived molecular constants using the formula,

$$I_{\text{b}} = \mu_{\text{c}} R^2 + (1/2) \langle 1 + \cos^2 \theta \rangle I_{\text{HCN}}, \quad (6)$$

where I_{b} is the moment of inertia of the complex calculated from the observed rotational constant, I_{HCN} is the moment of inertia of the HCN part, $\mu_{\text{c}} = m_{\text{H}_2} m_{\text{HCN}} / (m_{\text{H}_2} + m_{\text{HCN}})$ is the reduced mass, and $\langle \cos^2 \theta \rangle$ is calculated from the observed quadrupole coupling constant eqQ_0 . The H₂ part is treated as a free rotor.

We also observed the rotational transitions of the H₂-DCN isotopic species for both *ortho*- and *para*-H₂ species with the FTMW (for $J = 1-0$) and MMW (for $J = 3-2$, $4-3$, and $5-4$) spectrometers employed here. The average distances $\langle R \rangle$ between the centers of mass of H₂ and DCN subunits were derived from the rotational constants B_0 and the quadrupole coupling constants eqQ_0 due to the N nucleus in the same way as in the present Letter. The average distance $\langle R \rangle$ for (*o*)H₂-DCN (4.0034 Å) is longer by 0.0417 Å than that of (*o*)H₂-HCN. The difference is approximately equal to 0.0380 Å the calculated displacement of the center of mass of HCN by isotopic substitution, which definitively confirms that H₂ is attached to the N side of HCN in (*o*)H₂-HCN as reported in Ref. [1]. The results of H₂-DCN will be published separately.

Finally, observation of pure rotational spectra of H₂ containing complexes is of great importance because they are possible candidates for radio-astronomical detection, especially in a planetary atmosphere like the H₂-H₂ dimer in Jupiter [30]. In fact, radio-astronomical search of the H₂-CO complex has been attempted towards the TMC-1 molecular cloud, although it turned out unsuccessful [31]. The H₂-HCN complex has an advantage over H₂-CO, because the dipole moment of the former would be much larger than that of the latter. The $J = 1-0$ rotational transition frequencies for both the *para*-H₂ and *ortho*-H₂ species measured in the present

Letter will facilitate the detection of the H₂-HCN complex in the interstellar space.

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