Observation of the v1 fundamental band of DCNH+

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Gaussian instrument function. By adjusting the values of the spectroscopic constants $\bar{v}_0$, $\overline{B}_1$, and $\overline{C}_1$ for best agreement between the computed $|\chi^{(3)}|$ and the reduced data, we found the following results: vibrational origin frequency $\bar{v}_0 = 3004.8 \pm 0.2$ cm^{-1}, $\overline{B}_1 - \overline{B}_0 = -0.085 \pm 0.002$ cm^{-1}, and $\overline{C}_1 - \overline{C}_0 = -0.048 \pm 0.002$ cm^{-1}.

This experimental value of the ν_1 origin may be compared with prior estimates of 3044 cm^{-1} from a Urey–Bradley force field analysis,[3] 2992.6 cm^{-1} from a model anharmonic potential calculation,[16] and ~ 3220 and 3067 cm^{-1} from *ab initio* computations.[17,18] Knowledge of the actual frequency will allow a more realistic mapping of this potential surface. The decreases in rotational constants found on excitation of the $v = 1$ level in ν_1 are comparable in size to those measured for the ν_3 vibration.[6] By combining these rotational constant changes with the ground state $\overline{B}$ and $\overline{C}$ values, we obtain for the ν_1 mode: $\overline{B}_1 = 9.493$ cm^{-1} and $\overline{C}_1 = 4.694$ cm^{-1}.

In summary, we have measured the origin frequency of the last undetermined vibrational fundamental of the methyl radical in what we believe is the first reported use of CARS to obtain new spectroscopic constants of a transient polyatomic species. Despite the lack of resonant signal enhancement, this method provides a selective and reasonably sensitive probe for gas phase methyl which may be preferable to absorption spectroscopy in some applications. The method's high time resolution also suggests related dynamical studies of azomethane's photodissociation mechanism and collisional relaxation in the methyl fragment, both of which are in progress.

[1] G. Herzberg and J. Shoosmith, Can. J. Phys. **34**, 523 (1956).

[2] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **47**, 5146 (1967).

[3] A. Snelson, J. Phys. Chem. **74**, 537 (1970).

[4] L. Y. Tan, A. M. Winer, and G. C. Pimentel, J. Chem. Phys. **57**, 4028 (1972).

[5] C. Yamada, E. Hirota, and K. Kawaguchi, J. Chem. Phys. **75**, 5256 (1981).

[6] T. Amano, P. F. Bernath, C. Yamada, Y. Endo, and E. Hirota, J. Chem. Phys. **77**, 5284 (1982).

[7] H. Hermann and S. R. Leone, J. Chem. Phys. **76**, 4759 (1982).

[8] O. P. Strausz, J. W. Lown, and H. E. Gunning, Comp. Chem. Kinet. **5**, 568 (1972).

[9] For a review, see: J. W. Nibler and G. V. Knighten, in *Raman Spectroscopy of Gases and Liquids*, edited by A. Weber (Springer, Berlin, 1979), p. 253.

[10] L. A. Rahn, L. J. Zych, and P. L. Mattern, Opt. Commun. **30**, 249 (1979).

[11] R. B. Weisman, J. I. Selco, P. L. Holt, and P. A. Cahill, Rev. Sci. Instrum. **54**, 284 (1983).

[12] P. L. Holt, K. E. McCurdy, and R. B. Weisman (to be published).

[13] F. P. Jahn, J. Am. Chem. Soc. **59**, 1761 (1937).

[14] G. Herzberg, *Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1945), pp. 406–411.

[15] V. I. Fabelinsky, B. B. Krynetsky, L. A. Kulevsky, V. A. Mishin, A. M. Prokhorov, A. D. Savelev, and V. V. Smirnov, Opt. Commun. **20**, 389 (1977); R. L. Farrow, P. L. Mattern, and L. A. Rahn, Appl. Opt. **21**, 3119 (1982).

[16] V. Spirko and P. R. Bunker, J. Mol. Spectrosc. **95**, 381 (1982).

[17] D. M. Chipman, J. Chem. Phys. **78**, 3112 (1983).

[18] P. Botschwina, J. Flesch, W. Meyer, Chem. Phys. **74**, 321 (1983).

Observation of the ν_1 fundamental band of DCNH+

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Although HCNH+ has not been detected in interstellar space, it is widely recognized that HCNH+ is an important species in chemistry in interstellar clouds.[1] Recently Altman, Crofton, and Oka[2] succeeded in detecting the ν_1 (N–H stretch) and the ν_2 (C–H stretch) vibrational bands of this ion using a difference frequency laser spectrometer, and gave a prediction of the $J = 1$–0 rotational transition frequency with an accuracy of ± 6 MHz.

Interstellar observations[3] show a much higher DCN/HCN ratio than expected from cosmic abundance ratio for D and H. Watson[4] suggested the following two step mechanism:

$$\text{HCNH}^+ + \text{HD} \rightarrow \text{DCNH}^+ + \text{H}_2,$$

$$\text{DCNH}^+ + e \rightarrow \text{DCN} + \text{H}$$
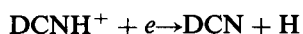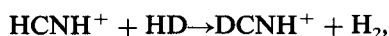
for the deuterium fractionation. Therefore, detection of the deuterated species of this ion in interstellar space is as important as the detection of HCNH+ itself. The present infrared observation gives the rotational constant almost as accurate

as that from microwave spectroscopy, and it will be of great use for search of this deuterated species by radio observation.

The second motivation to do this work was that the bond lengths of this basic ion cannot be determined accurately enough to compare with recent state-of-the-art *ab initio* calculations without obtaining the rotational constants of isotopically substituted species. This work is the first of a series aiming toward this goal.

The difference frequency laser system used here is similar to that described in Ref. 5. The discharge amplitude modulation technique in our previous experiments on HCO+6 and H$_2$D+7 was used also in this work. The DCNH+ was generated by a modulated dc discharge through a mixture of DCN (about 80 mTorr) and H$_2$ (about 900 mTorr). The purity of DCN used in this experiment was checked to be better than 98%. This reaction produces HCNH+ in addition to DCNH+. The peak discharge current of about 100 mA through a 2.5 cm diameter discharge tube was found to be optimum for production of DCNH+. At higher discharge
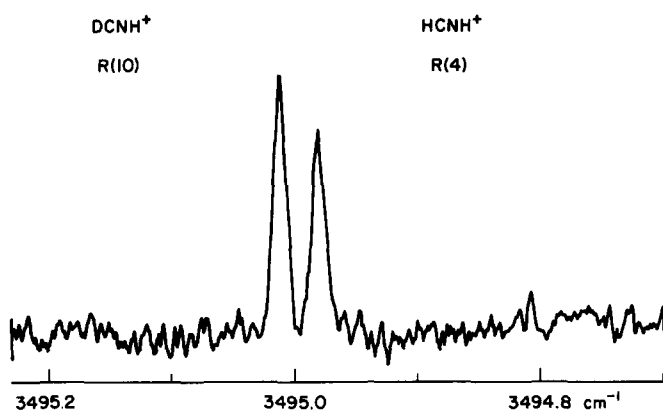
FIG. 1. The absorption lines of $DCNH^+$ and $HCNH^+$ recorded with a time constant of 0.4 s. The reaction conditions were optimized for production of $DCNH^+$.

TABLE II. Spectroscopic constants of $DCNH^+$ (in cm^{-1}).

	$v_1 = 1$ state	Ground state
v_0	3473.103 92 (21)	
B	1.022 905 (12)	1.028 265 (11)
$D \times 10^6$	1.149 (21)	1.151 (18)
Calculated	$v_0 = $ 3 495 [a]	
	$B_e = $ 1.011,[b] 1.035	$(B_0 = 1.026)$[c]

[a] Reference 9.
[b] Reference 10.
[c] Reference 11.

currents, the concentration of $HCNH^+$ increased. It suggests that $HCNH^+$ was produced in a secondary reaction between HCN and H_3^+. The discharge tube was immersed into an oil bath, and the oil was cooled by water through a heat exchanger. One difficulty encountered in this particular experiment was low infrared power around 3480 cm^{-1}. In this range, the power was less than 10% compared with the power in the adjacent range. This is thought to be due to impurity, probably water, trapped in the $LiNbO_3$ crystal. By chance, the band origin is just in this frequency range, and the low J-, P-, and R-branch lines were hard to observe partly due to their low intensity, and partly due to low power of the laser.

TABLE I. Transition wave numbers of the v_1 fundamental band of $DCNH^+$ (in cm^{-1}).

	v	$(o-c) \times 10^4$		v	$(o-c) \times 10^4$
$P(1)$	3471.0457	−17	$R(0)$	3475.1502	5
$P(2)$	68.9799	−3	$R(1)$	77.1848	0
$P(3)$	66.9004	−19	$R(2)$	79.2083	−8
$P(4)$	64.8143	5	$R(3)$	81.2227	2
$P(5)$	62.7150	3	$R(4)$	83.2257	5
$P(6)$	60.6047	−2	$R(5)$	85.2178	8
$P(7)$	58.4840	−7	$R(6)$	87.1982	3
$P(8)$	56.3549	10	$R(7)$	89.1681	2
$P(9)$	54.2134	8	$R(8)$	91.1285	15
$P(10)$	52.0618	9	$R(9)$	93.0755	5
$P(11)$	49.8996	9	$R(10)$	95.0112	−9
$P(12)$	47.7257	−4	$R(11)$	96.9377	−5
$P(13)$	45.5428	−3	$R(12)$	98.8520	−13
$P(14)$	43.3499	2	$R(14)$	3502.6507	6
$P(15)$	41.1458	−2	$R(16)$	06.4022	−2
$P(16)$	38.9315	−6	$R(18)$	10.1101	2
$P(17)$	36.7085	7	$R(19)$	11.9469	0
$P(18)$	34.4733	0			
$P(19)$	32.2281	−5			
$P(20)$	29.9734	−3			
$P(21)$	27.7085	−2			
$P(22)$	25.4328	−7			
$P(24)$	20.8537	8			

Table I lists the observed transition wave numbers together with obs–calc of the least squares fit. The transition wave numbers were calibrated with N_2O as reference.[8] The spectroscopic constants obtained from the fit are listed in Table II, and are compared to some calculated values. As seen in the table, the agreements are excellent.

The microwave transition frequencies can be calculated by using the rotational and the centrifugal distortion constants. However, the first three lowest rotational transition frequencies ($J = 1$–0, 2–1, 3–2) are overlapped by strong atmospheric O_2 or H_2O absorption lines. It is almost impossible to observe the interstellar $DCNH^+$ using these transitions at least with a ground based telescope. So the lowest rotational transition which is usable for detection of interstellar $DCNH^+$ is the $J = 4$–3 transition of which frequency is 246 604.0 $\pm$ 2.6 MHz, where the uncertainty denotes one standard error.

[1] E. Herbst and W. Klemperer, Astrophys. J. **185**, 505 (1973); E. Herbst, ibid. **222**, 508 (1978).

[2] R. S. Altman, M. W. Crofton, and T. Oka, J. Chem. Phys. **80**, 3911 (1984); (private communication).

[3] K. B. Jefferts, A. A. Penzias, and R. W. Wilson, Astrophys. J. **179**, L57 (1973); R. W. Wilson, A. A. Penzias, K. B. Jefferts, and P. M. Solomon, ibid. **179**, L107 (1973).

[4] W. D. Watson, Astrophys. J. **188**, 35 (1974).

[5] T. Amano, Bull. Soc. Chim. Belg. **92**, 565 (1983).

[6] T. Amano, J. Chem. Phys. **79**, 3595 (1983).

[7] T. Amano and J. K. G. Watson, J. Chem. Phys. **81**, 2869 (1984).

[8] C. Amiot and G. Guelachvili, J. Mol. Spectrosc. **59**, 171 (1976); C. Amiot, ibid. **59**, 191 (1976).

[9] P. Botschwina (private communication).

[10] D. J. DeFrees, G. H. Loew and A. D. McLean, Astrophys. J. **257**, 376 (1982).

[11] P. S. Dardi and C. E. Dykstra, Astrophys. J. **240**, L171 (1980).