THE INFRARED SPECTRUM OF CN IN ITS GROUND ELECTRONIC STATE

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Dedicated to Professor Rudolf Zahradník on the occasion of his 75th birthday.

$^{12}C^{14}N$ vibration-rotation bands for the sequences (1-0) through (9-8) were observed in the spectral region 1800–2200 cm^{-1} using a Bruker 120 HR Fourier transform spectrometer at an unapodized resolution of 0.027 cm^{-1}. Of the 362 lines observed, the wavenumbers of 237 lines were least-squares fitted using the Dunham expansion coefficients with a root-mean-square deviation of 0.00093 cm^{-1}. Together with most accurate data from the literature, the data were also fitted in the framework of the reduced potential curve (RPC) method. The global potential energy function resulting from this fit provides a fairly quantitative description of the experimental data, at least up to 30 000 cm^{-1}. In addition to global fitting, the RPC approach was also used for fully quantitative fitting of the data pertaining to the lowest three vibrational states. The effective potential energy curves obtained in this way allow for very accurate predictions of highly excited rotational states.

Keywords: Rotation-vibration; CN radical; Cyanides; IR spectroscopy; Vibrational spectroscopy; Reduced potential curve; *Ab initio* calculations; Rotational states.

The CN radical is observed in interstellar molecular clouds and atmospheres of stars, planets and comets. It is also significant in numerous laboratory processes at high temperatures (flames, chemical reactions, discharges) where it is often formed from trace amounts of carbon and nitrogen. Moreover, it also serves as a prototype molecule for various molecular calculations. Thus, not surprisingly, the radical is one of the most frequently studied radicals in the literature. The radical is a very strong absorber/emitter of radiation and its spectra, extending from the vacuum UV far into the infrared without significant gaps, provide a very useful tool for its detection

and monitoring. A vast portion of the available spectral data arises from the $A^2\Pi \rightarrow X^2\Sigma^+$ and $B^2\Pi \rightarrow X^2\Sigma^+$ electronic transitions[1–7] and the infrared transitions in the $X^2\Sigma^+$ ground electronic state[8]. From the point of view of the vibrational excitation, the most important information is obtained from vibronic data involving vibrational levels up to $v = 18$. Such high vibrational excitation corresponds to temperatures well above 10 000 K thus indicating the potential use of CN in high temperature monitoring on the one hand, and, on the other, the possibility of experimental determination of a sizable part of the molecular potential energy function. Coverage of the rotational excitation by the available data, however, is not as complete. The vibronic data[1–7] exhibit sizable "rotational" gaps for some vibrational states (see, *e.g.*, Table I of ref.[4]), the vibrational data[8] include vibrational levels only up to $v = 4$, and, the purely rotational data[9–12] include lowly excited states only.

The aim of this study is to improve the coverage of the ro-vibrational data for CN and to determine its "experimental" potential energy function over a wide range of vibrational displacements. For this purpose, we have concentrated primarily on measuring the wavenumbers of as many lines as possible in the system of the ($v' \rightarrow v''$) transitions which is covered by our spectral facilities. The "global" potential energy function was constructed by "morphing" the *ab initio* potential of Polák and Fišer[13] within the framework of the reduced potential curve method of Jenč[14,15].

EXPERIMENTAL

The spectra (Fig. 1) were recorded from the emission of the positive column of a glow discharge plasma with a Bruker 120 HR Fourier transform high-resolution interferometer equipped with an InSb detector. The dicharge glass tube was 20 cm long with an inner diameter of 12 mm. The DC discharge was maintained by a high voltage applied to two stainless steel electrodes (Fig. 2). The smaller anode was oriented closer to the entry iris of the spectrometer. To reduce the electric and sputtering noise signal, the (cylindric glass-metal sheet) cathode was chosen to be much larger than the anode. The voltage drop across the discharge was 700 V and the discharge current was 50 mA.

The radiation from the discharge plasma was focused by a CaF_2 lens into the entering iris of the FT spectrometer.

The plasma made from a mixture of cyanogen $(CN)_2$ and helium was cooled by flowing water or liquid nitrogen in the outer jacket of the cell. The best conditions for generating the CN radical in its doublet sigma ground state were found to be P(He) = 670 Pa and $P(CN)_2$ = 1.3 Pa (all pressures measured with the cell at room temperature).

The recording spectral range was about 1800–4000 cm^{-1}, at an unapodized resolution of 0.027 cm^{-1}. The recording number of scans was about 50 to obtain a reasonable signal-to-noise ratio. Lines of CO and CO_2 present in the spectra as impurities were used for calibration of the line positions[16].

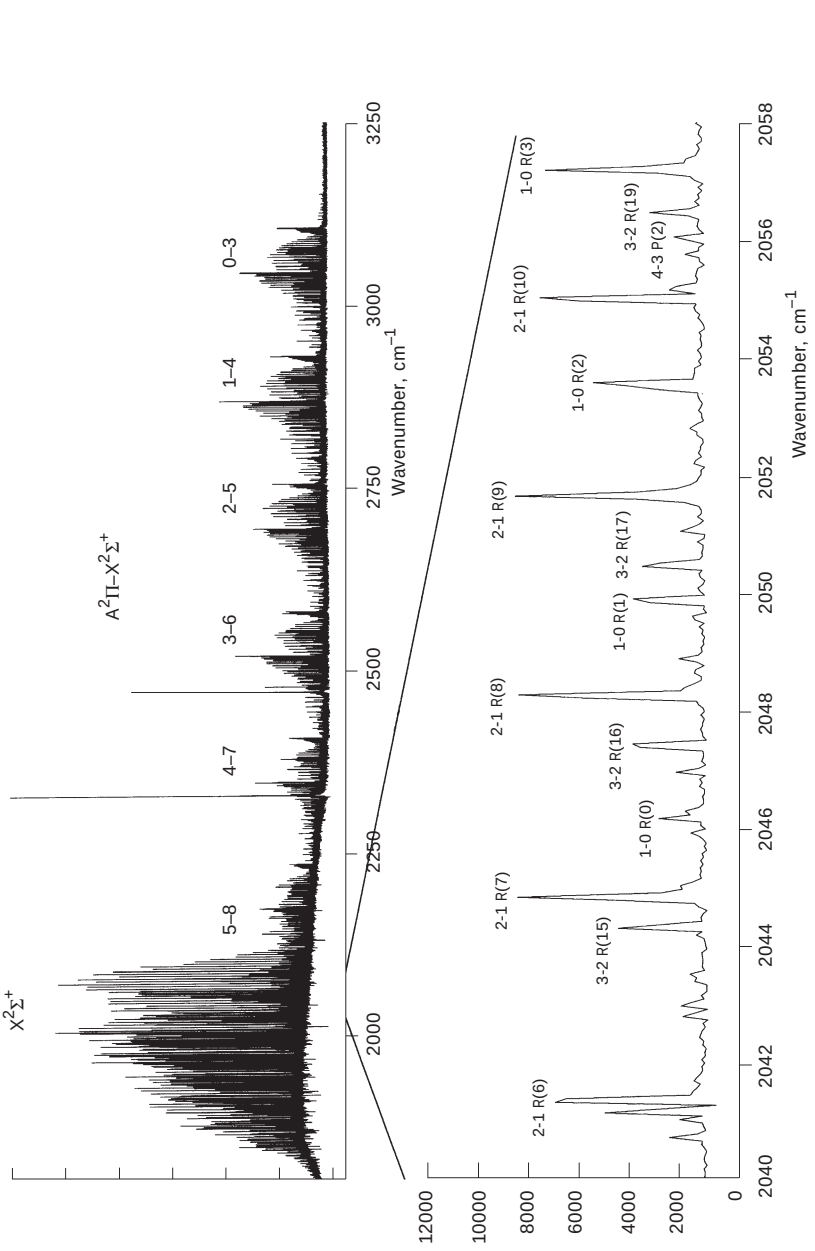

FIG. 1
The emission spectrum of the CN radical in the spectral range 3–5 μm

The post-zero filled spectrum and accumulated line profiles were analyzed using the Bruker OPUS software.

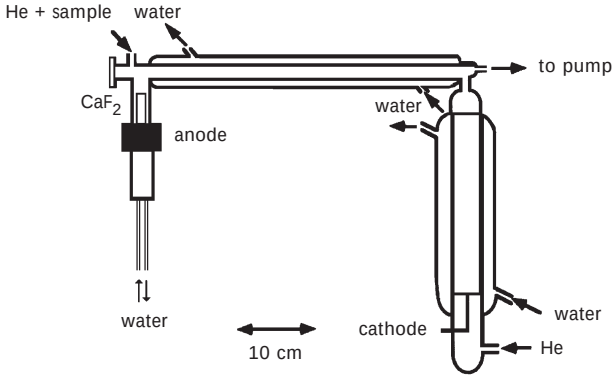

FIG. 2
The emission discharge tube used in this study

THEORETICAL

The pointwise calculated *ab initio* energies[13] were smoothed (by a quantitative least-squares fitting) using the following potential energy function

$$U(r) = \sum_p F_p \left\{ 1 - \mathrm{e}^{-a(r-r_r)-b(r-r_r)^2-c(r-r_r)^3} \right\}^p + C_3 / r^3 + U_0 \,, \qquad (1)$$

where r is the internuclear distance and a, b, c, F_p, r_r, C_3 and U_0 are the fitting parameters. The (non-zero) fitted parameters acquire the following values: F_2 = 336 356.9232 cm^{-1}, F_3 = –455 074.6558 cm^{-1}, F_5 = 423 814.5472 cm^{-1}, F_6 = –51 851.5415 cm^{-1}, F_7 = –423 688.2621 cm^{-1}, F_8 = 231 712.3366 cm^{-1}, C_3 = –2744.6231 cm^{-1} Å^3, r_r = 1.176949 Å, a = 1.095 Å^{-1}, b = 0.1714 Å^{-2}, c = 0.6543 Å^{-3}. The corresponding theoretical ro-vibrational energies were found as eigenvalues of the radial Hamiltonian (the hyperfine interactions are disregarded as they are too small to be resolved with the present resolution)

$$H^{\mathrm{rv}} = -\frac{\hbar}{2\mu}\frac{d^2}{dr^2} + U(r) + \frac{\hbar^2}{2\mu r^2} N(N+1) \,, \qquad (2)$$

where $\hbar$ is the Planck constant, μ is the reduced mass and N is the rotational quantum number. The reduced potential curve scheme used in the present paper has the following (generalized) form (see, *e.g.*, refs[14,15])

$$u = \frac{U}{D_e}, \tag{3}$$

$$\rho = \frac{r - \left\{1 - \alpha \exp\left[-\beta(1+\gamma r)r / \rho_{ij}\right]\right\}\rho_{ij}}{r_e - \left\{1 - \alpha \exp\left[-\beta(1+\gamma r)r / \rho_{ij}\right]\right\}\rho_{ij}}, \tag{4}$$

$$\rho_{ij} = \frac{r_e - \left(\kappa D_e / k_e\right)^{1/2}}{\left\{1 - \alpha \exp\left[-\beta(1+\gamma r)r / \rho_{ij}\right]\right\}\rho_{ij}}, \quad \kappa = 3.96, \tag{5}$$

where ρ, u and U are the reduced internuclear distance, the reduced energy and the genuine potential, respectively; D_e, r_e, and k_e are the depth of the minimum of the potential curve, the equilibrium internuclear distance, and the harmonic force constant, respectively; κ is the universal "reduced" force constant; α, β and γ are "correction" parameters (in the standard RPC formula, $\alpha = 1$, $\beta = 1$ and $\gamma = 0$).

RESULTS AND DISCUSSION

The recorded spectrum consists predominatly of the fundamental transition ($1 \rightarrow 0$) and of a series of ($v + 1 \rightarrow v$) hot bands (spectrally profound vibrational levels ranging from $v = 0$ to $v = 8$, see Fig. 1). Energetically, the observed states span only the lowest, fairly harmonic part of the total potential. Consequently, all the observed transitions can be expected to be closely describable by means of the conventional Dunham expansion analysis. As a matter of fact (Tables I and II), this expectation is fully confirmed by the actual analysis. As we can see in Table I, the fitted lines are reproduced quantitatively using quite moderate number of the Dunham coefficients (it should be stressed that only well isolated and reasonable intensive lines were respected in the fitting). In the table we can also see that the fit of our purely infrared data is in a perfect agreement with the fit in which we fixed the "rotational" Dunham coefficients at their values obtained from fitting very accurate rotational data taken from ref.[10]. Fairly less quantitative agreement, however, was achieved in comparing our results with the fit based on the "vibronic" data[5]. Thus, instead of attempting a global Dunham expansion analysis which would include these (less accurate) data, we found it worthwhile to fit the available data in terms of a global potential energy function (GPEF).

TABLE I
Observed and calculated lines (in cm^{-1}) of $^{12}C^{14}N$

$\tilde{\nu}_{obs}$	J'	J''	v'	v''	o-c[b]	o-c[c]	o-c[d]	$\tilde{\nu}_{obs}$	J'	J''	v'	v''	o-c[b]	o-c[c]	o-c[d]
2046.1731	1	0	1	0	0.0012	0.0006	0.0090	2049.8840	2	1	1	0	–0.0003	–0.0008	0.0074
2053.5619	3	2	1	0	0.0004	0.0000	0.0077	2057.2034	4	3	1	0	0.0000	–0.0004	0.0064
2060.8098	5	4	1	0	0.0000	–0.0003	0.0049	2064.3806	6	5	1	0	0.0001	–0.0003	0.0026
2067.9153	7	6	1	0	–0.0002	–0.0006	–0.0009	2071.4142	8	7	1	0	–0.0004	–0.0007	–0.0054
2074.8768	9	8	1	0	–0.0007	–0.0010	–0.0144	2078.3038	10	9	1	0	–0.0004	–0.0007	–0.0181
2081.6943	11	10	1	0	–0.0001	–0.0004	–0.0264	2085.0476	12	11	1	0	–0.0006	–0.0008	–0.0371
2088.3645	13	12	1	0	–0.0006	–0.0009	–0.0494	2091.6447	14	13	1	0	–0.0005	–0.0008	–0.0635
2094.8878	15	14	1	0	–0.0005	–0.0008	–0.0798	2098.0937	16	15	1	0	–0.0004	–0.0007	–0.0985
2101.2625	17	16	1	0	–0.0002	–0.0003	–0.1195	2104.3954	18	17	1	0	0.0017	0.0016	–0.1414
2107.4877	19	18	1	0	0.0006	0.0006	–0.1692	2110.5439	20	19	1	0	0.0013	0.0014	–0.1982
2112.5613	21	20	1	0	0.0011	0.0015	–0.2311	2116.5377	22	21	1	0	–0.0019	–0.0014	–0.2703
2119.4735[a]	23	22	1	0	–0.0073	–0.0064	–0.3151	2122.3717[a]	24	23	1	0	–0.0119	–0.0106	–0.3627
2125.2563[a]	25	24	1	0	0.0086	0.0103	–0.3891	2128.1161[a]	26	25	1	0	0.0430	0.0452	–0.4054
2130.8628[a]	27	26	1	0	0.0032	0.0060	–0.4999	2133.5737[a]	28	27	1	0	–0.0333	–0.0298	–0.5955
2038.6415	0	1	1	0	–0.0008	–0.0015	0.0069	2034.8172[a]	1	2	1	0	–0.0081	–0.0090	–0.0003
2030.9735	2	3	1	0	–0.0003	–0.0013	0.0078	2027.0870	3	4	1	0	–0.0010	–0.0020	0.0081
2023.1678	4	5	1	0	–0.0001	–0.0012	0.0104	2019.2137	5	6	1	0	0.0000	–0.0012	0.0128
2015.2257	6	7	1	0	0.0001	–0.0012	0.0160	2011.2042	7	8	1	0	0.0005	–0.0009	0.0207
2007.1483	8	9	1	0	0.0001	–0.0013	0.0257	2003.0601	9	10	1	0	0.0008	–0.0006	0.0334
1998.9378	10	11	1	0	0.0008	–0.0007	0.0417	1994.7822	11	12	1	0	0.0005	–0.0008	0.0517
1990.5944	12	13	1	0	0.0011	–0.0002	0.0642	1986.3719	13	14	1	0	–0.0002	–0.0014	0.0769
1982.1188	14	15	1	0	0.0006	–0.0004	0.0939	1977.8299[a]	15	16	1	0	–0.0019	–0.0026	0.1099
1973.5134	16	17	1	0	0.0003	–0.0001	0.1332	1969.1610	17	18	1	0	–0.0011	–0.0011	0.1554
1964.7830[a]	18	19	1	0	0.0039	0.0044	0.1869	1960.3640	19	20	1	0	–0.0002	0.0009	0.2122
1955.9139[a]	20	21	1	0	–0.0036	–0.0018	0.2412	1951.4403	21	22	1	0	0.0010	0.0036	0.2817
1946.9344[a]	22	23	1	0	0.0048	0.0083	0.3246	1942.3878	23	24	1	0	–0.0009	0.0038	0.3617
1937.8149	24	25	1	0	–0.0017	0.0042	0.4074	1933.2020[a]	25	26	1	0	–0.0116	–0.0043	0.4479
1928.5855[a]	26	27	1	0	0.0057	0.0146	0.5196	2019.8438	1	0	2	1	0.0005	0.0005	0.0028
2023.5209	2	1	2	1	0.0003	0.0004	0.0025	2027.1632	3	2	2	1	0.0006	0.0007	0.0024
2030.7691	4	3	2	1	0.0001	0.0001	0.0008	2034.3397	5	4	2	1	–0.0005	–0.0003	–0.0012
2037.8752	6	5	2	1	–0.0003	0.0000	–0.0033	2041.3746	7	6	2	1	–0.0002	0.0000	–0.0065
2044.8378	8	7	2	1	–0.0003	–0.0001	–0.0110	2048.2649	9	8	2	1	–0.0003	–0.0001	–0.0166
2051.6558	10	9	2	1	–0.0002	0.0001	–0.0235	2055.0098	11	10	2	1	–0.0004	–0.0001	–0.0323
2058.3277	12	11	2	1	0.0000	0.0003	–0.0422	2061.6090	13	12	2	1	0.0006	0.0009	–0.0538
2064.8485[a]	14	13	2	1	–0.0037	–0.0033	–0.0722	2068.0587	15	14	2	1	0.0000	0.0004	–0.0850
2071.2298	16	15	2	1	0.0018	0.0023	–0.1019	2074.3594	17	16	2	1	–0.0004	0.0002	–0.1254
2077.4544	18	17	2	1	0.0004	0.0011	–0.1485	2080.5117	19	18	2	1	0.0013	0.0022	–0.1744
2083.5320[a]	20	19	2	1	0.0030	0.0042	–0.2022	2086.5050[a]	21	20	2	1	–0.0044	–0.0030	–0.2425
2089.4503	22	21	2	1	–0.0013	0.0004	–0.2754	2092.3576	23	22	2	1	0.0022	0.0043	–0.3115
2095.2542[a]	24	23	2	1	0.0335	0.0361	–0.3232	2098.0491	25	24	2	1	0.0018	0.0049	–0.4017
2100.8117[a]	26	25	2	1	–0.0233	–0.0195	–0.4776	2103.5892[a]	27	26	2	1	0.0055	0.0100	–0.5036
2106.2607[a]	28	27	2	1	–0.0325	–0.0272	–0.6006	2108.9338[a]	29	28	2	1	–0.0296	–0.0233	–0.6611
2111.5424[a]	30	29	2	1	–0.0517	–0.0444	–0.7511	2114.2053[a]	31	30	2	1	0.0201	0.0287	–0.7519
2012.3840	0	1	2	1	0.0005	0.0004	0.0027	2008.6006	1	2	2	1	–0.0007	–0.0009	0.0016
2004.7752[a]	2	3	2	1	–0.0092	–0.0095	–0.0065	2000.9327	3	4	2	1	–0.0004	–0.0008	0.0032

TABLE I
(*Continued*)

$\tilde{\nu}_{obs}$	J'	J''	v'	v''	o-c[b]	o-c[c]	o-c[d]	$\tilde{\nu}_{obs}$	J'	J''	v'	v''	o-c[b]	o-c[c]	o-c[d]
1997.0467	4	5	2	1	–0.0007	–0.0012	0.0043	1993.1274	5	6	2	1	–0.0001	–0.0007	0.0072
1989.1737	6	7	2	1	0.0001	–0.0006	0.0105	1985.1861	7	8	2	1	0.0003	–0.0005	0.0150
1981.1653	8	9	2	1	0.0010	0.0002	0.0212	1977.1091	9	10	2	1	–0.0002	–0.0010	0.0269
1973.0215	10	11	2	1	0.0007	–0.0001	0.0362	1968.8991	11	12	2	1	0.0000	–0.0008	0.0457
1964.7432	12	13	2	1	–0.0011	–0.0018	0.0566	1960.5572	13	14	2	1	0.0007	0.0001	0.0724
1956.3365	14	15	2	1	0.0005	0.0000	0.0884	1952.0832	15	16	2	1	0.0004	0.0001	0.1068
1947.7994[a]	16	17	2	1	0.0022	0.0022	0.1296	1943.4779	17	18	2	1	–0.0013	–0.0010	0.1497
1939.1278	18	19	2	1	–0.0013	–0.0005	0.1762	1934.7503[a]	19	20	2	1	0.0034	0.0046	0.2102
1930.3330	20	21	2	1	0.0000	0.0019	0.2394	1925.8873	21	22	2	1	0.0000	0.0026	0.2751
1921.4114	22	23	2	1	0.0013	0.0048	0.3156	1916.8967[a]	23	24	2	1	–0.0048	–0.0004	0.3523
1912.3507[a]	24	25	2	1	–0.0110	–0.0054	0.3926	1993.4751	1	0	3	2	–0.0010	–0.0007	0.0064
1997.1204[a]	2	1	3	2	0.0022	0.0025	0.0095	2000.7248	3	2	3	2	–0.0001	0.0002	0.0067
2004.2952	4	3	3	2	–0.0009	–0.0005	0.0050	2007.8314	5	4	3	2	–0.0001	0.0003	0.0042
2011.3309	6	5	3	2	–0.0002	0.0002	0.0017	2014.7942	7	6	3	2	–0.0005	–0.0001	–0.0019
2018.2215	8	7	3	2	–0.0006	–0.0003	–0.0064	2021.6128	9	8	3	2	–0.0003	–0.0001	–0.0118
2024.9676	10	9	3	2	–0.0001	0.0001	–0.0187	2028.2849	11	10	3	2	–0.0008	–0.0006	–0.0280
2031.5668	12	11	3	2	0.0000	0.0002	–0.0377	2034.8172[a]	13	12	3	2	0.0062	0.0063	–0.0437
2038.0184	14	13	3	2	0.0003	0.0004	–0.0640	2041.1879	15	14	3	2	0.0000	0.0001	–0.0808
2044.3201	16	15	3	2	–0.0002	–0.0001	–0.0999	2047.4164	17	16	3	2	0.0013	0.0014	–0.1197
2050.4704	18	17	3	2	–0.0018	–0.0016	–0.1469	2053.4899	19	18	3	2	–0.0015	–0.0012	–0.1734
2056.4728	20	19	3	2	0.0002	0.0007	–0.2015	2059.4119[a]	21	20	3	2	–0.0037	–0.0030	–0.2383
2062.3248[a]	22	21	3	2	0.0046	0.0056	–0.2663	2065.1719[a]	23	22	3	2	–0.0144	–0.0131	–0.3250
2068.0104[a]	24	23	3	2	–0.0034	–0.0016	–0.3572	2070.7981[a]	25	24	3	2	–0.0043	–0.0020	–0.4051
2073.5051[a]	26	25	3	2	–0.0470	–0.0441	–0.4987	2076.2609	27	26	3	2	–0.0017	0.0019	–0.5084
2078.9582[a]	28	27	3	2	0.0244	0.0288	–0.5415	2081.5644	29	28	3	2	–0.0012	0.0041	–0.6307
2084.1264[a]	30	29	3	2	–0.0314	–0.0250	–0.7290	1986.0849	0	1	3	2	–0.0014	–0.0013	0.0059
1982.3364[a]	1	2	3	2	–0.0026	–0.0026	0.0048	1978.5553	2	3	3	2	–0.0016	–0.0016	0.0062
1974.7401	3	4	3	2	0.0000	–0.0002	0.0086	1970.8884	4	5	3	2	–0.0005	–0.0008	0.0096
1967.0031	5	6	3	2	–0.0003	–0.0007	0.0120	1963.0831	6	7	3	2	–0.0007	–0.0012	0.0148
1959.1301	7	8	3	2	0.0000	–0.0006	0.0197	1955.1433	8	9	3	2	0.0006	–0.0001	0.0258
1951.1218	9	10	3	2	0.0003	–0.0005	0.0323	1947.0669	10	11	3	2	0.0001	–0.0008	0.0404
1942.9789	11	12	3	2	0.0002	–0.0008	0.0506	1938.8586	12	13	3	2	0.0011	0.0001	0.0635
1930.5166	14	15	3	2	0.0007	–0.0002	0.0931	1926.2969	15	16	3	2	0.0010	0.0001	0.1118
1922.0434	16	17	3	2	0.0001	–0.0007	0.1318	1917.7724[a]	17	18	3	2	0.0141	0.0135	0.1694
1913.4396	18	19	3	2	–0.0014	–0.0017	0.1802	1967.0700	1	0	4	3	0.0014	0.0017	0.0156
1970.6745	2	1	4	3	–0.0008	–0.0006	0.0132	1974.2471	3	2	4	3	0.0005	0.0008	0.0140
1977.7820	4	3	4	3	–0.0002	0.0001	0.0124	1981.2823	5	4	4	3	0.0004	0.0006	0.0113
1984.7451	6	5	4	3	–0.0006	–0.0004	0.0079	1988.1732	7	6	4	3	–0.0001	0.0000	0.0050
1991.5644	8	7	4	3	–0.0003	–0.0002	0.0004	1994.9192	9	8	4	3	–0.0003	–0.0004	–0.0054
1998.2386	10	9	4	3	0.0008	0.0007	–0.0115	2001.5185	11	10	4	3	–0.0008	–0.0010	–0.0218
2004.7751[a]	12	11	4	3	0.0112	0.0109	–0.0203	2007.9730	13	12	4	3	0.0016	0.0012	–0.0423
2011.1463[a]	14	13	4	3	0.0046	0.0042	–0.0537	2014.2751	15	14	4	3	0.0005	0.0000	–0.0744
2017.3701	16	15	4	3	0.0001	–0.0004	–0.0937	2020.4280	17	16	4	3	0.0004	–0.0001	–0.1149
2023.4488	18	17	4	3	0.0014	0.0009	–0.1381	2026.4283	19	18	4	3	–0.0009	–0.0013	–0.1673
2029.3747	20	19	4	3	0.0018	0.0016	–0.1945	2032.2860[a]	21	20	4	3	0.0078	0.0077	–0.2216

TABLE I
(*Continued*)

$\tilde{\nu}_{obs}$	J'	J''	v'	v''	o-c[b]	o-c[c]	o-c[d]	$\tilde{\nu}_{obs}$	J'	J''	v'	v''	o-c[b]	o-c[c]	o-c[d]
2035.1494[a]	22	21	4	3	0.0044	0.0045	–0.2614	2037.9720	23	22	4	3	–0.0013	–0.0008	–0.3068
2040.7559[a]	24	23	4	3	–0.0068	–0.0059	–0.3558	2043.5171[a]	25	24	4	3	0.0040	0.0053	–0.3922
2046.2237	26	25	4	3	–0.0008	0.0011	–0.4481	2048.8977	27	26	4	3	0.0010	0.0037	–0.5013
1959.7519[a]	0	1	4	3	0.0028	0.0029	0.0169	1956.0374	1	2	4	3	0.0007	0.0008	0.0149
1952.2885	2	3	4	3	–0.0009	–0.0009	0.0137	1948.5072	3	4	4	3	–0.0002	–0.0003	0.0153
1944.6911	4	5	4	3	0.0003	0.0001	0.0172	1940.8393	5	6	4	3	–0.0005	–0.0008	0.0187
1936.9546	6	7	4	3	0.0001	–0.0004	0.0224	1933.0352	7	8	4	3	0.0002	–0.0005	0.0266
1925.0944	9	10	4	3	–0.0001	–0.0010	0.0386	1921.0744	10	11	4	3	0.0008	–0.0003	0.0478
1917.0201	11	12	4	3	0.0008	–0.0005	0.0578	1912.9321	12	13	4	3	0.0005	–0.0009	0.0694
1908.8107	13	14	4	3	–0.0001	–0.0015	0.0827	1904.6590	14	15	4	3	0.0021	0.0006	0.1009
1900.4697	15	16	4	3	–0.0005	–0.0020	0.1167	1896.2530[a]	16	17	4	3	0.0023	0.0007	0.1403
1891.9962[a]	17	18	4	3	–0.0025	–0.0040	0.1590	1887.6986[a]	18	19	4	3	–0.0157	–0.0171	0.1720
1883.3974	19	20	4	3	–0.0002	–0.0014	0.2167	1879.0565[a]	20	21	4	3	0.0077	0.0067	0.2568
1940.6144[a]	1	0	5	4	–0.0044	–0.0044	0.0132	1944.1887	2	1	5	4	–0.0015	–0.0014	0.0159
1947.7257	3	2	5	4	–0.0002	–0.0001	0.0168	1951.2274	4	3	5	4	0.0016	0.0017	0.0176
1954.6896	5	4	5	4	–0.0001	–0.0001	0.0142	1958.1176	6	5	5	4	0.0000	0.0000	0.0119
1961.5093	7	6	5	4	0.0002	0.0001	0.0087	1964.8646	8	7	5	4	0.0003	0.0002	0.0043
1968.1830	9	8	5	4	0.0001	–0.0001	–0.0016	1971.4660	10	9	5	4	0.0012	0.0010	–0.0076
1974.7401[a]	11	10	5	4	0.0303	0.0301	0.0127	1977.9176	12	11	5	4	–0.0001	–0.0004	–0.0282
1981.0874	13	12	5	4	–0.0011	–0.0014	–0.0415	1984.2228	14	13	5	4	0.0009	0.0006	–0.0538
1987.3204[a]	15	14	5	4	0.0026	0.0023	–0.0687	1990.3789[a]	16	15	5	4	0.0029	0.0026	–0.0874
1993.3984	17	16	5	4	0.0019	0.0018	–0.1098	1996.3794	18	17	5	4	0.0005	0.0005	–0.1353
1999.3226	19	18	5	4	–0.0006	–0.0005	–0.1634	2002.2282	20	19	5	4	–0.0011	–0.0006	–0.1937
2005.1024[a]	21	20	5	4	0.0055	0.0063	–0.2201	2007.9237[a]	22	21	5	4	–0.0022	–0.0010	–0.2641
2010.7229[a]	23	22	5	4	0.0067	0.0084	–0.2949	2013.4075[a]	24	23	5	4	–0.0600	–0.0578	–0.4050
2016.1979[a]	25	24	5	4	0.0181	0.0210	–0.3740	2018.8718[a]	26	25	5	4	0.0190	0.0226	–0.4242
1933.3707	0	1	5	4	0.0008	0.0008	0.0184	1929.6927	1	2	5	4	0.0001	0.0000	0.0178
1925.9797	2	3	5	4	–0.0006	–0.0007	0.0175	1922.2334	3	4	5	4	0.0003	0.0001	0.0193
1918.4500	4	5	5	4	–0.0012	–0.0016	0.0192	1914.6344	5	6	5	4	–0.0004	–0.0008	0.0223
1910.7842	6	7	5	4	0.0002	–0.0003	0.0261	1906.8983	7	8	5	4	–0.0006	–0.0013	0.0295
1902.9792	8	9	5	4	–0.006	–0.0014	0.0350	1899.0268	9	10	5	4	0.0000	–0.0009	0.0425
1895.0415	10	11	5	4	0.0016	0.0006	0.0524	1891.0186	11	12	5	4	–0.0009	–0.0020	0.0600
1886.9652	12	13	5	4	–0.0004	–0.0016	0.0724	1882.8797	13	14	5	4	0.0013	0.0000	0.0881
1878.7577	14	15	5	4	–0.0004	–0.0017	0.1025	1874.5996[a]	15	16	5	4	–0.0051	–0.0065	0.1162
1870.4164[a]	16	17	5	4	–0.0022	–0.0035	0.1400	1866.2023[a]	17	18	5	4	0.0026	0.0013	0.1683
1861.9471	18	19	5	4	–0.0013	–0.0024	0.1908	1857.6627[a]	19	20	5	4	–0.0019	–0.0029	0.2194
1853.3519[a]	20	21	5	4	0.0032	0.0025	0.2569	1914.1238	1	0	6	5	–0.0013	–0.0016	0.0151
1917.6601	2	1	6	5	–0.0008	–0.0010	0.0155	1921.1622	3	2	6	5	0.0013	0.0011	0.0171
1924.6259	4	3	6	5	0.0009	0.0007	0.0158	1928.0538	5	4	6	5	0.0008	0.0006	0.0140
1931.4453	6	5	6	5	0.0004	0.0003	0.0114	1934.8021	7	6	6	5	0.0018	0.0016	0.0094
1938.1189	8	7	6	5	–0.0003	–0.0004	0.0029	1941.4018	9	8	6	5	0.0003	0.0003	–0.0021
1947.8548	11	10	6	5	–0.0005	–0.0003	–0.0185	1951.0282	12	11	6	5	0.0017	0.0020	–0.0266
1954.1597	13	12	6	5	–0.0008	–0.0003	–0.0412	1957.2567	14	13	6	5	–0.0002	0.0005	–0.0549
1960.3161	15	14	6	5	0.0003	0.0013	–0.0707	1963.3356	16	15	6	5	–0.0012	0.0000	–0.0910
1966.3226[a]	17	16	6	5	0.0026	0.0042	–0.1084	1972.1678[a]	19	18	6	5	–0.0040	–0.0015	–0.1656

TABLE I
(*Continued*)

$\tilde{\nu}_{obs}$	J'	J''	v'	v''	o-c[b]	o-c[c]	o-c[d]	$\tilde{\nu}_{obs}$	J'	J''	v'	v''	o-c[b]	o-c[c]	o-c[d]
1975.0354[a]	20	19	6	5	–0.0048	–0.0018	–0.1960	1977.8728[a]	21	20	6	5	0.0027	0.0065	–0.2212
1980.6772[a]	22	21	6	5	–0.0160	0.0205	–0.2440	1983.4130	23	22	6	5	–0.0005	0.0049	–0.2999
1986.1304[a]	24	23	6	5	0.0036	0.0100	–0.3388	1988.8102[a]	25	24	6	5	0.0094	0.0168	–0.3799
1906.9448[a]	0	1	6	5	0.0021	–0.0025	0.0143	1903.3036	1	2	6	5	–0.0012	–0.0016	0.0154
1899.6268	2	3	6	5	–0.0008	–0.0012	0.0163	1895.9158	3	4	6	5	0.0004	–0.0001	0.0184
1892.1679	4	5	6	5	–0.0005	–0.0010	0.0191	1888.3869	5	6	6	5	0.0002	–0.0003	0.0221
1884.5728[a]	6	7	6	5	0.0022	0.0017	0.0274	1880.7213	7	8	6	5	0.0013	0.0007	0.0308
1876.8354	8	9	6	5	0.0001	–0.0004	0.0352	1872.9162	9	10	6	5	–0.0003	–0.0009	0.0417
1864.9779	11	12	6	5	0.0004	–0.0001	0.0613	1860.9559[a]	12	13	6	5	–0.0016	–0.0021	0.0713
1856.9055	13	14	6	5	0.0013	0.0009	0.0884	1852.8143[a]	14	15	6	5	–0.0032	–0.0035	0.1002
1848.6991	15	16	6	5	0.0013	0.0012	0.1234	1844.5397[a]	16	17	6	5	–0.0054	–0.0054	0.1378
1887.5802[a]	1	0	7	6	–0.0053	–0.0060	0.0081	1891.0880[a]	2	1	7	6	0.0024	0.0018	0.0157
1894.5505	3	2	7	6	0.0007	0.0001	0.0135	1897.9789	4	3	7	6	0.0009	0.0004	0.0129
1901.3698	5	4	7	6	–0.0002	–0.0006	0.0103	1904.7246	6	5	7	6	–0.0010	–0.0013	0.0072
1908.0437	7	6	7	6	–0.0011	–0.0013	0.0039	1911.3281	8	7	7	6	0.0008	0.0008	0.0015
1914.5755[a]	9	8	7	6	0.0025	0.0027	–0.0023	1917.7724[a]	10	9	7	6	–0.0093	–0.0089	–0.0210
1920.9524	11	10	7	6	–0.0009	–0.0003	–0.0210	1924.0855[a]	12	11	7	6	–0.0022	–0.0012	–0.0324
1927.1844	13	12	7	6	–0.0001	0.0012	–0.0424	1930.2394[a]	14	13	7	6	–0.0045	–0.0027	–0.0607
1933.2620[a]	15	14	7	6	–0.0034	–0.0012	–0.0759	1936.2485	16	15	7	6	–0.0006	0.0022	–0.0916
1939.1858[a]	17	16	7	6	–0.0089	–0.0056	–0.1209	1942.1069[a]	18	17	7	6	0.0048	0.0088	–0.1308
1944.9719	19	18	7	6	0.0007	0.0056	–0.1613	1947.7994	20	19	7	6	–0.0023	0.0035	–0.1936
1950.5953	21	20	7	6	0.0018	0.0085	–0.2220	1876.8761[a]	1	2	7	6	0.0045	0.0038	0.0181
1873.2297	2	3	7	6	0.0002	–0.0006	0.0143	1869.5497	3	4	7	6	–0.0027	–0.0035	0.0124
1865.8429[a]	4	5	7	6	0.0025	0.0018	0.0192	1862.0958[a]	5	6	7	6	0.0023	0.0016	0.0214
1858.3114	6	7	7	6	–0.0006	–0.0013	0.0218	1854.4941	7	8	7	6	–0.0020	–0.0036	0.0249
1850.6460	8	9	7	6	0.0002	–0.0004	0.0328	1846.7576[a]	9	10	7	6	–0.0038	–0.0043	0.0359
1842.8405[a]	10	11	7	6	–0.0025	–0.0028	0.0459	1838.8903	11	12	7	6	–0.0004	–0.0006	0.0584
1834.9072[a]	12	13	7	6	0.0025	0.0025	0.0736	1830.8573[a]	13	14	7	6	–0.0279	–0.0277	0.0575
1860.9559[a]	1	0	8	7	–0.0423	–0.0434	–0.0272	1864.4642	2	1	8	7	0.0018	0.0007	0.0167
1867.8652[a]	3	2	8	7	–0.0254	–0.0264	–0.0109	1871.2807	4	3	8	7	–0.0019	–0.0029	0.0117
1874.6404	5	4	8	7	0.0022	0.0012	0.0142	1877.9579	6	5	8	7	0.0006	–0.0004	0.0102
1881.2390	7	6	8	7	–0.0008	–0.0018	0.0055	1884.4849	8	7	8	7	–0.0006	–0.0015	0.0014
1887.6986[a]	9	8	8	7	0.0044	0.0036	0.0008	1890.8615[a]	10	9	8	7	–0.0043	–0.0050	–0.0150
1893.9942[a]	11	10	8	7	–0.0059	–0.0065	–0.0251	1897.0903[a]	12	11	8	7	–0.0066	–0.0072	–0.0362
1900.1581	13	12	8	7	0.0019	0.0015	–0.0399	1903.1714[a]	14	13	8	7	–0.0063	–0.0065	–0.0623
1906.1642	15	14	8	7	0.0028	0.0029	–0.0695	1909.1000[a]	16	15	8	7	–0.0069	–0.0065	–0.0980
1912.0119	17	16	8	7	–0.0024	–0.0016	–0.1147	1914.8826	18	17	8	7	–0.0007	0.0006	–0.1368
1853.9552[a]	0	1	8	7	–0.0071	–0.0083	0.0080	1850.3724[a]	1	2	8	7	–0.0185	–0.0197	–0.0033
1846.7576[a]	2	3	8	7	–0.0266	–0.0278	–0.0109	1843.1407	3	4	8	7	–0.0014	–0.0027	0.0152
1839.4649	4	5	8	7	–0.0001	–0.0015	0.0181	1835.7451[a]	5	6	8	7	–0.0078	–0.0093	0.0126
1832.0105[a]	6	7	8	7	0.0044	0.0029	0.0282	1828.2782[a]	7	8	8	7	0.0536	0.0520	0.0817
1824.4058[a]	8	9	8	7	–0.0028	–0.0045	0.0308	1820.5594	9	10	8	7	0.0011	–0.0007	0.0417
1816.6909[a]	10	11	8	7	0.0171	0.0152	0.0662								

[a] Lines exluded from fitting. [b] Fitted to the data obtained in this study (RMS deviation 0.00093 cm^{-1}). [c] Fitted to the data obtained in this study with fixing the rotational Dunham coefficients from ref.[10] (RMS deviation 0.00148 cm^{-1}). [d] Calculated using the Dunham coefficients of ref.[5]

On the contrary to the Dunham (polynomial) expansion analysis, accurate determination of GPFE allows not only for a physically correct prediction of the highly excited states, but also for evaluation of the pertinent wavefunctions and, consequently, for a physically correct rationalization of all the molecular properties. One of the most flexible GPFEs available in the literature for diatomic molecules is the so-called reduced potential curve (RCP) as suggested and elaborated by Jenč and his collaborators (for details, see, *e.g.*, refs[14,15]). The RCP approach can be applied in various ways. The application adopted in this study is based on a numerical morphing of the recent *ab initio* potential of ref.[13] within the framework of the above described theoretical scheme. The first step of this morphing consists of constructing the standard reduced potential curve RPC ($\alpha = 1$, $\beta = 1$ and $\gamma = 0$) from the *ab initio* potential energy curve. In the second step, we construct a global potential so that its generalized reduced potential curve GRPC (α, β and γ being free parameters) coincides with the *ab initio* RPC and provides the best least-squares description of the fitted data.

TABLE II
The Dunham coefficients Y_{ij} of $^{12}C^{14}N$ in its ground electronic state (in cm^{-1})[a]

Y_{ij}	Fit 1[b]	Fit 2[c]	Ref.[5,d]
Y_{10}	2068.68302(55)	2068.68469(60)	2068.648(11)
Y_{20}	–13.11965(26)	–13.12027(29)	–13.0971(68)
Y_{30}	–0.005793(46)	–0.005715(51)	–0.0124(17)
Y_{40}	–0.0000762(26)	–0.0000789(29)	0.00070(18)
$Y_{50} \times 10^4$			–0.323(68)
Y_{01}	1.8998291(53)	1.89978300(15)	1.89978316(67)
Y_{11}	–0.0173783(22)	–0.01737160(24)	–0.0173720(12)
$Y_{12} \times 10^7$		–0.170(57)	
$Y_{21} \times 10^4$	–0.2391(90)	–0.2582(12)	–0.2586(56)
$Y_{31} \times 10^6$		–0.266(20)	–0.211(99)
$Y_{02} \times 10^5$	–0.64873(70)	–0.64034(83)	
$Y_{41} \times 10^5$	–0.0416(58)	–0.00104(11)	–0.00161(57)
$Y_{51} \times 10^5$	0.0077(10)		
$Y_{61} \times 10^7$	–0.0425(53)		

[a] Standard deviations are given in parenthesis in units of the last quoted decimal. [b] Obtained fitting the data recorded in this study. [c] Obtained fitting the data recorded in this study with fixing the "rotational" Dunham coefficients of ref.[10]. [d] Obtained in ref.[5]

To obtain an insight into the prospects and limitations of this approach, we performed a series of model calculations. Representative results of this modelling, labelled as Fits 1–6, are collected in Tables III and IV. To enable comparisons, Table IV also contains the results obtained using the Dunham expansion approach. The calculated energies, E_v, are given relative to the energies obtained in Fit 5 (*i.e.*, *e.g.*, E_v(Fit 1) ≈ Fit 1 + Fit 5). The Fit 5 ("reference") energies were obtained by fitting all the available infrared experimental wavenumbers and the v = 14 and 16 vibrational band centers derived from the available vibronic bands in ref.[6].

The first presented fit (Fit 1) is based on processing our v = 0–8 experimental data. As we can see in Table III, the pertinent potential describes our data fairly accurately, RMS deviation being only 0.0061 cm^{-1}, and predicts higher lying vibrational energies which are in a reasonable harmony with the reference energies (see Table IV). In addition to the "global" fitting of experimental data, the RPC approach may also be used for "local" fittings based on information pertaining to only a limited number of molecular states. As we can see in Tables III and IV, such fits (Fits 2 and 3) can provide a very close description of the fitted data, but not necessarily reasonable predictions for states lying well outside the range of the fitted energies. Nevertheless, the quality of this fitting appears to be comparable to that obtained by the standard polynomial approach, and can thus be used as its vi-

TABLE III
Parameters[a] of the generalized reduced potential curves obtained by fitting to the experimental data of $^{12}C^{14}N$

Fit	r_e, Å	ρ_{ij}, Å	D_e, cm^{-1}	α	β	γ	rms[b]
Fit 1[c]	1.17181331(629)	0.741457(176)	66433.9(135)	1.181641(968)	1.178829(637)	0.0	0.0061
Fit 2[d]	1.17181465(173)	0.84706990(313)	59740.0[e]	1.0	1.0	0.0	0.0010
Fit 3[f]	1.17181028(255)	0.7377830(235)	66700.0	1.200938(259)	1.191926(189)	0.0	0.0042
Fit 4[g]	1.171808	0.842853(672)	63441	1.15169(559)	1.124235(497)	–0.13[e]	0.0516
Fit 5[h]	1.1718120(145)	0.806568(321)	64694.4(157)	1.226504(935)	1.306315(812)	–0.12[e]	0.0264
Fit 6[i]	1.1718359(282)	0.79249(221)	65449(125)	1.26052(560)	1.33659(478)	–0.12[e]	0.0527
Ab initio	1.171629	0.813085	62963.2	1.0	1.0	0.0	0.0

[a] Standard deviations are given in parenthesis in units of the last quoted decimal. [b] Root-mean-square deviation. [c] Present data with v = 0–8. [d] Present data with v = 0–1. [e] Fixed after a preliminary determination. [f] Comprising present data with v = 0–2 and data from ref.[8]. [g] Comprising all present (v = 0–9) data, D_e and r_e fixed at their experimental values taken from refs[5,17]. [h] Comprising all present (v = 0–9) data, data from ref.[8] and the v = 14 and 16 vibrational band centers from ref.[6]. [i] Comprising all present (v = 0–9) data, data from ref.[8], rotational data from refs[9–12] and "smoothed" ro-vibrational data from refs[5–7]

TABLE IV
Vibrational energies[a] (in cm^{-1}) of $^{12}C^{14}N$ evaluated by means of the fitted GRPC potentials (Fits 1–5), Dunham coefficients (DC 1–5) and *ab initio* potential (AI)

v	Fit 5	Fit 1	Fit 2	Fit 3	Fit 4	Fit 6	DC 1[b]	DC 2[c]	DC 3[d]	DC 4[e]	AI
1	2042.41	0.03	0.02	0.02	–0.03	0.02	0.02	0.01	0.01	0.03	2.00
2	4058.54	0.03	0.28	0.01	–0.02	0.01	0.01	0.01	0.01	0.03	4.66
3	6048.35	0.01	0.72	–0.01	0.02	–0.01	–0.01	–0.02	–0.01	0.01	7.92
4	8011.80	0.00	1.25	–0.03	0.06	–0.03	–0.03	–0.05	–0.04	–0.01	11.7
5	9948.82	–0.02	1.79	–0.05	0.09	–0.05	–0.04	–0.08	–0.05	–0.02	16.1
6	11859.37	–0.02	2.28	–0.04	0.10	–0.05	–0.02	–0.09	–0.05	–0.01	20.9
7	13743.38	0.01	2.62	0.01	0.07	–0.03	0.04	–0.07	–0.01	0.03	26.2
8	15600.81	0.07	2.74	0.11	–0.02	0.03	0.15	–0.01	0.08	0.10	31.9
9	17431.60	0.19	2.55	0.27	–0.18	0.13	0.33	0.06	0.22	0.20	37.9
10	19235.72	0.37	1.98	0.52	–0.43	0.29	0.59	0.12	0.42	0.33	44.2
11	21013.11	0.62	0.94	0.86	–0.78	0.52	0.92	0.09	0.68	0.48	50.7
12	22763.74	0.96	–0.64	1.31	–1.25	0.82	1.32	–0.10	0.99	0.63	57.5
13	24487.59	1.40	–2.85	1.89	–1.86	1.21	1.78	–0.58	1.35	0.74	64.4
14	26184.63	1.96	–5.77	2.62	–2.63	1.69	2.28	–1.51	1.72	0.79	71.4
15	27854.84	2.64	–9.49	3.50	–3.57	2.28	2.81	–3.09	2.09	0.73	78.5
16	29498.21	3.47	–14.1	4.56	–4.70	2.99	3.33	–5.58	2.43	0.51	85.6
17	31114.73	4.46	–19.7	5.83	–6.03	3.83	3.83	–9.24	2.72	0.09	92.7
18	32704.38	5.63	–26.4	7.31	–7.60	4.81	4.28	–14.4	2.92	–0.59	100
19	34267.14	7.01	–34.3	9.05	–9.43	5.95	4.65	–21.5	3.02	–1.58	106
20	35802.97	8.62	–43.6	11.1	–11.5	7.25	4.94	–30.9	3.01	–2.92	113
21	37311.84	10.5	–54.5	13.4	–14.0	8.75	5.17	–43.1	2.88	–4.62	119
22	38793.67	12.7	–67.2	16.1	–16.8	10.5	5.35	–58.6	2.68	–6.69	125
23	40248.35	15.2	–82.0	19.3	–20.0	12.4	5.56	–78.0	2.46	–9.09	131
24	41675.74	18.2	–99.1	22.9	–23.7	14.6	5.91	–102	2.34	–11.8	135
25	43075.64	21.7	–119	27.1	–27.9	17.2	6.55	–130	2.46	–14.6	139
26	44447.78	25.8	–142	32.1	–32.8	20.0	7.72	–165	3.07	–17.4	142
27	45791.81	30.6	–170	37.8	–38.4	23.3	9.72	–205	4.45	–19.9	144
28	47107.30	36.3	–201	44.6	–44.9	27.1	13.0	–253	7.01	–21.7	144
29	48393.68	43.0	–239	52.5	–52.4	31.4	17.9	–307	11.3	–22.4	143
30	49650.26	51.0	–283	61.9	–61.2	36.4	25.3	–370	17.9	–21.3	139

[a] Relative to the Fit 5 data. [b] Ref.[2] [c] Ref.[5] [d] Ref.[8] [e] This work.

able alternative, especially for experimental data involving only moderately excited rotational states. In such cases, although quantitative, the standard polynomial fittings may not allow for a physically correct determination of the higher centrifugal distortion constants preventing thus accurate prediction of highly excited rotational states.

In Table III we can also see that the "global" fits (Fits 1 and 5) provide dissociation energies, D_e, significantly exceeding the "best" experimental estimate D_e = 63 441 cm^{-1} (ref.[17]). Interestingly, the value D_e = 64 694 cm^{-1} pertaining to the reference Fit 5 coincides closely with the estimate D_e = 64 750–65 550 cm^{-1} obtained by Sauval, Blomme, and Grevesse[18] from the solar CN ↔ C + N equilibrium abundances. This estimate, however, is inconsistent with the most recent experimental determinations (see ref.[17] and references therein). Thus, we also found it worthwhile to perform our calculations with D_e fixed at its "best" experimental value. The corresponding fit, Fit 4, describes our experimental data with only slightly lower accuracy than the reference fit. The differences in the latter fits become sizable only for $v > 16$ evidencing thus inadequacy of our procedure to determine D_e with accuracy which would be better than ≈1000 cm^{-1}. The last presented fit in this study (see Fit 6 in Tables III–V) resulted from our aim to probe consistency of the previously fitted ro-vibrational and purely vibrational data with the rotational data pertaining to the "vibronic" transitions involving the $v > 9$ vibrational states. The data were incorporated into the fitting directly in the form of combination differences, *i.e.*, without any smoothing which obscures deficiences of the individual experimental data. The actual calculations revealed the quite complete consistency of our $v < 10$ infrared data with the $v \geq 10$ vibronic data from ref.[3]. Agreement with other sources of the $v > 10$ data was not as complete; for instance, while we found quite reasonable harmony between our data and the $v = 16$ data of ref.[6], the $v = 14$ data from the same reference exhibit considerable disagreement with our predictions (for details see Table V). Interestingly, gradual discarding of the profoundly "inconsistent" vibronic data from our fitting procedure led to a very similar potential energy curve as in the cases with fitting to only purely vibrational data (compare Fit 6 with Fits 1 and 3 in Table IV). Thus, as the discarded data constitute only a minor part of the total input, we take it as a strong evidence for the physical correctness of all the fitted "global" potentials over the probed energy region and their adequacy for correct predicting outside this region and theoretical rationalization of the usual spectroscopic constants (dispersion of the predicted quantities may be taken as realistic estimates of the pertinent "confidence limits"). Asymptotically, of course, our predictions diverge and may become

TABLE V
Spectroscopic constants (in cm^{-1}) of $^{12}C^{14}N$

v	*Ab initio*			Fit 5			Exp		
	B_v	$D_v \times 10^6$	$H_v \times 10^{10}$	B_v	$D_v \times 10^6$	$H_v \times 10^{10}$	B_v	$D_v \times 10^6$	Ref.
0	1.891726	6.40302		1.891057	6.40842		1.891084	6.40176	12
0	1.891727	6.40742	0.0738	1.891058	6.41278	0.0723			
1	1.874401	6.40540		1.873625	6.41713		1.873666	6.41677	12
2	1.857040	6.41001		1.856160	6.42767		1.856188	6.43118	9
3	1.839635	6.41679		1.838656	6.43998		1.838653	6.44679	11
4	1.822180	6.42573		1.821105	6.45405		1.821060	6.46180	11
5	1.804667	6.43674		1.803503	6.46981		1.803405	6.47681	11
6	1.787091	6.44979		1.785846	6.48722		1.785685	6.49182	11
7	1.769447	6.46479		1.768128	6.50616		1.767899	6.50684	11
8	1.751731	6.48165		1.750347	6.52660		1.750041	6.52185	11
9	1.733939	6.50026		1.732499	6.54838		1.733269	6.53686	11
10	1.716067	6.52054		1.714583	6.57144		1.714048	6.55187	11
10	1.716067	6.52292	0.0396	1.714584	6.57432	0.0493			
11	1.698114	6.54242		1.696597	6.59569		1.69593	6.756	5
12	1.680077	6.56579		1.678540	6.62105				
13	1.661956	6.59071		1.660412	6.64750				
14	1.643747	6.61719		1.642210	6.67502		1.64248	6.65	7
							1.6388	5.80	7
							1.6273	6.60	6
15	1.625449	6.64539		1.623936	6.70368		1.62282	6.8	7
16	1.607059	6.67551		1.605587	6.73364		1.6042	6.6	6
17	1.588573	6.70793		1.587161	6.76512		1.58737	6.42	7
18	1.569983	6.74324		1.568655	6.79851		1.56353	3.26	7
19	1.551282	6.78217		1.550063	6.83435				
20	1.532456	6.82572		1.531377	6.87334				
20	1.532456	6.82440	–0.0219	1.531377	6.87349	0.0056			
21	1.513488	6.87519		1.512586	6.91641				
22	1.494356	6.93218		1.493674	6.96472				
23	1.475030	6.99876		1.474622	7.01973				
24	1.455472	7.07743		1.455403	7.08323				
25	1.435635	7.17130		1.435985	7.15736				
26	1.415461	7.28414		1.416326	7.24473				
27	1.394876	7.42065		1.396378	7.34853				
27	1.394874	7.40720	–0.2232	1.396377	7.33977	–0.1457			
28	1.373792	7.58671		1.376078	7.47258				
28	1.373790	7.56942	–0.2869	1.376076	7.46142	–0.1803			
29	1.352099	7.78970		1.355352	7.62161				
29	1.352096	7.76751	–0.3681	1.355350	7.60716	–0.2317			
30	1.329662	8.03916		1.334110	7.80143				
30	1.329657	8.01066	–0.4729	1.334108	7.78287	–0.2988			
32	1.281837	8.68455	–0.7865	1.289615	8.25410	–0.5122			
34	1.228397	9.75021	–1.3582	1.241399	8.96161	–0.8439			
36	1.166065	11.53854	–2.5351	1.187600	10.06066	–1.4366			
38	1.088623	14.87263	–5.4961	1.125126	11.86889	–2.6348			
40	0.981727	22.46401	–16.2288	1.048230	15.15492	–5.5522			
42	0.798797	48.82641	–101.7862	0.944161	22.31831	–15.4638			

TABLE VI
Potential energy function, $U(R)$, of CN[a]

R_{C-N}, Å	$U(R)$, cm^{-1}	R_{C-N}, Å	$U(R)$, cm^{-1}	R_{C-N}, Å	$U(R)$, cm^{-1}
0.814224	125323.34	1.114438	1539.85	1.456522	18086.60
0.824571	115023.86	1.124564	1019.63	1.508274	22779.66
0.834894	105432.32	1.134692	614.34	1.560236	27424.48
0.845195	96497.88	1.144824	316.75	1.612407	31930.88
0.855476	88175.70	1.154958	120.02	1.664790	36236.80
0.865739	80425.80	1.165097	17.69	1.717380	40299.44
0.875984	73212.13	1.175239	3.64	1.770175	44087.14
0.886214	66501.96	1.185386	72.09	1.823169	47573.30
0.896429	60265.26	1.195537	217.56	1.876357	50733.07
0.906631	54474.33	1.205693	434.88	1.929731	53543.46
0.916822	49103.45	1.215854	719.15	1.983285	55986.35
0.927002	44128.64	1.226020	1065.73	2.037010	58052.93
0.937172	39527.42	1.236192	1470.24	2.090898	59747.84
0.947334	35278.69	1.246370	1928.53	2.144940	61091.31
0.957487	31362.53	1.256553	2436.68	2.199127	62118.29
0.967634	27760.16	1.266742	2990.96	2.253451	62874.73
0.977776	24453.85	1.276938	3587.85	2.307904	63412.10
0.987911	21426.77	1.287140	4224.04	2.362477	63781.46
0.998043	18663.03	1.297349	4896.35	2.417163	64028.72
1.008171	16147.56	1.307565	5601.81	2.471952	64191.70
1.018295	13866.06	1.317787	6337.58	2.526839	64299.21
1.028417	11804.99	1.328017	7101.00	2.581817	64371.60
1.038538	9951.52	1.338253	7889.52	2.636880	64422.29
1.048657	8293.51	1.348497	8700.75	2.692022	64459.56
1.058776	6819.42	1.358748	9532.43	2.747238	64488.25
1.068894	5518.34	1.369007	10382.39	2.802524	64511.17
1.079013	4379.92	1.379274	11248.62	2.857876	64529.94
1.089133	3394.40	1.389548	12129.19	2.913293	64545.48
1.099253	2552.49	1.399829	13022.29	2.968771	64558.39
1.109376	1845.42	1.430722	15760.15	3.024310	64569.28

[a] Derived in Fit 5.

meaningless. Improving the dissociation asymptotics of the fitted potential energy function would require involving of accurate data of the so far unprobed states, the higher v the better. The present version of the fitted potential in its "reference" form is collected in Table VI (a more detailed representation of this or other potentials fitted in this is available by "inverting" Eqs (*3*)–(*5*) with respect to r and U).

CONCLUSIONS

A sequence of highly resolved rotation-vibration ($v + 1 \rightarrow v$) bands with $v \leq 9$ was recorded for $^{12}C^{14}N$. The data were fitted quantitatively using the standard Dunham expansion approach and the reduced potential curve approach of Jenč. The latter approach, based on morphing an *ab initio* potential energy curve, allowed determination of a highly accurate potential energy function of CN over a very wide region of the vibrational coordinate (see Table VI). Knowledge of this function allows for fairly quantitative prediction of the so far unknown molecular energies and physically correct rationalization of all the properties of the molecular states of all the molecular isotopomers in their electronic ground states. Moreover, the calculated data form a reliable basis for deeper re-analysis of the experimental spectra describing vibronic transitions originated in the electronic ground state.

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