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Radial Functions of the Molecule CH in the Electronic State X $^2\Pi_r$

J. F. Ogilvie and Frank Y. H. Wang (王一豪)
Academia Sinica, Institute of Atomic and Molecular Sciences
P.O. Box 23-166, Taipei, Taiwan 107, R.O.C.
and
Department of Chemistry, National Tsing Hua University,
Hsinchu, Taiwan 300, R. O. C.

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From published data for the vibration-rotational and electronic spectra of the CH free radical we have extracted the parameters of the radial functions in the range $0.87 < R/10^{-10}$ m< 1.61 to describe the potential energy, spin-orbital coupling, spin-rotational coupling and A-doubling effects (orbit-rotational coupling and spin uncoupling) in the ground electronic state X $^2\Pi_r$. These results we have used to predict the band parameters of the CD radical in the vibrational states $0 \leqslant v \leqslant 4$ of the ground electronic state.

I. INTRODUCTION

The most physically meaningful representation of the molecular spectra of molecules containing only two nuclei with their associated electrons, which is also the most compact representation, has the form of radial functions,[1] i.e. functions of which the argument is the internuclear separation R and which are formally independent of nuclear mass. This representation, which originated in the classical idea that such molecules consist of two atoms, was introduced[2] successfully into quantum mechanics, and thereby justified, first by Born and Oppenheimer and later by others in more comprehensive treatments.[3] Even the corrections consequent of this approximation can be analogously expressed as radial functions.[4,5] Not only the compactness of this form of representation makes it useful, but also there exists the possibility to predict the spectral properties of isotopic variants of the molecular species other than those for which experimental data have been measured. In the present work we have exploited precisely this capability in order to predict several band parameters of the CD ($^{12}C^2H$) free radical from the data known for the CH ($^{12}C^1H$) species.

The reactive molecule CH is important in both terrestrial and astrophysical contexts. In combustion processes and plasmas involving hydrocarbon reactants, the radical CH is an important intermediate species which in the presence of oxygen becomes eventually converted to carbon oxide (or carbon dioxide) and water. Since its first detection in 1918, the CH radical has been observed in such extraterrestrial environments as the solar and stellar atmospheres, comets and the interestellar medium.[6] In the laboratory, spectra have been measured in the microwave or far infrared, mid infrared, visible, near ultraviolet and vacuum ultraviolet regions, corresponding to pure rotational transitions, vibration-rotational transitions and electronic transitions between vibration-rotational states of different electronic states. As a result of these measurements,[7] many and fairly accurate band parameters exist for five vibrational states of the ground electronic state X $^2\Pi_r$ of CH. In contrast relatively few spectral lines have been reported for the CD species. Not only are the corresponding spectra of CD more difficult to detect because of the relative scarcity (or equivalently the greater cost) of deuterium, but the spectra would be more congested as a consequence of the relatively smaller values of almost all spectral parameters. For this reason accurately predicted spectral parameters of CD may assist in the detection and analysis of the new spectra that will eventually be measured.

II. THEORETICAL PROCEDURE

The treatment of the spectral data is based upon the representation of the vibration-rotational energies for each electronic state of a particular isotopic species in the_ general form[8]

$$E(v, J) = \sum_k \sum_\ell (Y_{k\ell} + Z_{k\ell})(v + \tfrac{1}{2})^k \, [J(J + 1)]^\ell$$

with as many coefficients $Y_{k\ell}$ and $Z_{k\ell}$ being taken as are required to reproduce satisfactorily the available data. The coefficients $Y_{k\ell}$ take into account the terms in the hamiltonian for the kinetic energy of the nuclei, the internuclear potential energy and the rotational motion of the nuclei about the centre of molecular mass. The coefficients $Z_{k\ell}$ take into account any further interactions. The vibration-rotational energies E(v,J) therefore implicitly depend on parameters in addition to the vibrational quantum number v and the quantum number J for total molecular angular momentum (apart from any intrinsic nuclear angular momenta which we ignore).

In the case of the ground electronic state of CH, the designation $^2\Pi_r$ implies the existence of net angular momentum due to both the orbital motion of the electrons about the internuclear axis and the net spin of the electrons. The pairwise coupling of these angular momenta consequently leads to spin-orbital, spin-rotational and orbit-rotational interactions; the uncoupling of the electronic spin angular momentum from the internuclear axis as the angular momentum due to molecular rotation increases also produces significant spectral effects. Therefore we have essentially five sets of spectral parameters. The vibrational energy T_v relative to the ground vibrational state, the principal rotational coefficient B_v and the centrifugal-distortion parameters D_v, H_v and L_v of a particular vibrational state, which are related to the vibration-rotational motions of the molecule, would be applicable to a diatomic molecule in any electronic state. As there is net angular momentum due to electronic spin, then the spin-rotational interaction leads to the parameter γ_v for the vibrational effects, and γ_{Dv} for the further rotational dependence of this interaction. Because the ground state of CH is a doublet state, there is net electronic spin due to effectively only one electron and therefore no spin-spin interaction with which to contend. As there exist both net spin and net orbital angular momenta of the electrons, the interaction between them requires terms involving both A_v for the vibrational dependence and A_{Dv} for the further rotational effects. For an electronic state $^1\Pi$, there is a coupling between the orbital angular momentum and the molecular rotation that leads to the parameters q_v for the vibrational dependence, q_{Dv} for the primary rotational dependence and q_{Hv} for further centrifugal effects. To take into account the uncoupling of the spin angular momenta from the internuclear axis, there exist correspondingly the parameters p_v, p_{Dv} and p_{Hv}. For the actual case of a $^2\Pi$ state, because the latter two effects are connected, one describes both p and q as A-doubling parameters. In the spectral analysis of a single isotopic species, the rotational dependence of the spin-orbital interaction, expressed in A_{Dv}, occurs inseparably with the vibrational dependence of the spin-rotational interaction, as γ_v;[9] however the mass dependence of rotational energies permits the extraction of the separate quantities if appropriate spectral data for an isotopic variant are available."

From the tabulated data of these band parameters,[7] we have fitted the coefficients $Y_{k\ell}$, and $Z_{k\ell}$ of several kinds, according to the method of general linear weighted regression,[11] in which the squared reciprocal of the estimated standard error of each value[7] of a particular quantity was used as the relative weight. By this means, from the values of T_v we produced values of Y_{k0}; B_v led to Y_{k1}, D_v to $Y_{k,2}$, H_v to $Y_{k,3}$ and L_v to $Y_{k,4}$. From the values of q_v we derived the values of $Z^q_{k,0}$; p_{Dv} led to $Z^q_{k,1}$ and p_{Hv} to $Z^q_{k,2}$. Analogously from the values of γ_v and γ_{Dv} we generated Z^γ_{k0} and Z^γ_{k1} respectively; from A_v resulted $Z^A_{k,0}$, and from p_v and p_{Dv} came Z^p_{k0} and Z^p_{k1}. For A_{Dv} only one value is available, for v = 0;[10] this we used as an approximate value of $Z^A_{0,1}$. For p_{Hv} values are lacking for other than v = 0, but this lack was inconsequential. The results of this analysis are presented in Table I.

The radial functions we expressed in terms of the argument $z \equiv 2(R-R_e)/(R+R_e)$,[12] which has the useful property of retaining finite values, specifically within the range $[-2,2]$ corresponding to the entire range of molecular existence, $0<R<\infty$.[13] The radial functions are of two types, both in the form of truncated series in z to non-negative powers; one is for potential energy,

$$V(z) = c_0 z^2 (1 + \sum_{j=1} c_j z^j)$$

of form exactly analogous to that, discussed by Dunham,[14] which has the argument $x \equiv (R-R_e)/R_e$ but which obviously suffers from ill behaviour as $R \rightarrow \infty$.[13] Both representations are most useful in the range near $R=R_e$, the equilibrium internuclear separation at which the potential energy has a minimum value, which for the ground electronic state

TABLE I. Spectral coefficients/m^{-1} $Y_{k\ell}$ and various $Z_{k\ell}$ of CH in the ground electronic state $X\,^2\Pi_r$.[a]

	$Y_{k\ell}$				
k/ℓ	0	1	2	3	4
0		1445.9795 ±0.0047	-0.14730460 $\pm 7.1\times 10^{-7}$	1.1438×10^{-5} $+1.7\times 10^{-8}$	-8.91×10^{-10} $\pm 0.17\times 10^{-10}$
1	286075.1256 ± 0.0019	− 53.6519 ±0.0092	0.0024727 $+1.3\times 10^{-6}$	4.79×10^{-7} $\pm 0.30\times 10^{-7}$	5.4×10^{-11} $+2.5\times 10^{-11}$
2	− 6443.9004 ± 0.0014	0.3304 ±0.0047	-5.558×10^{-5} $\pm 0.067\times 10^{-5}$	7.6×10^{-8} $+1.4\times 10^{-8}$	
3	36.3967 ±0.0016	-0.02112 ±0.00066	-7.733×10^{-6} $\pm 0.093\times 10^{-6}$	-1.46×10^{-8} $\pm 0.19\times 10^{-8}$	
4	-1.5418 ~0.0040				

k ℓ	$Z^A_{k\ell}$	$Z^\gamma_{k\ell}$	$Z^p_{k\ell}$	$Z^q_{k\ell}$
0 0	2805.119 ±0.037	-2.5859 ± 0.0029	3.490 ± 0.023	3.93845 ±0.00046
1 0	19.122 ± 0.075	0.1589 ±0.0011	− 0.213 ± 0.026	-0.14223 ±0.00102
2 0			0.0138 ± 0.0056	0.00158 ±0.00054
3 0				-0.000202 ~0.000079
0 1	0.05894 ±0.00026	4.225×10^{-4} $\pm 0.110\times 10^{-4}$	-9.34×10^{-4} $\pm 0.60\times 10^{-4}$	-1.5461×10^{-3} $\pm 0.0047\times 10^{-3}$
1 1		9.1×10^{-6} $+3.2\times 10^{-6}$	2.53×10^{-4} $\pm 0.53\times 10^{-4}$	4.78×10^{-5} $\pm 0.85\times 10^{-5}$
2 1				-5.5×10^{-6} $\pm 4.0\times 10^{-6}$
0 2			1.09×10^{-7} $\pm 0.18\times 10^{-7}$	3.100×10^{-7} $\pm 0.023\times 10^{-7}$
1 2				-2.61×10^{-8} $\pm 0.60\times 10^{-8}$

[a] In Tables I and II the indicated uncertainties correspond to one estimated standard error.

defines the zero of the energy scale. The coefficients c_j of this representation are defined by analytic relations” to the spectral coefficients $Y_{k\ell}$, from which the former are determined by an iterative process due to the nonlinear relationships. In fact the most reliable estimates of the potential-energy coefficients c_j result from the relatively precise spectral coefficients Y_{k0} and Y_{k1}; the remaining coefficients $Y_{k\ell}$, $\ell > 1$, serve however as tests of either the consistency of the spectral analysis or the absence of significant perturbations (nonadiabatic effects). The other function,

$$K^\alpha(z) = \sum_{j=0} h_j^\alpha z^j$$

in which α denotes A, γ, p or q depending on the particular application, is likewise best determined from the spectral coefficients Z^α_{k0} and Z^α_{k1}, according to the analytic relations previously reported,[8] but again any remaining data serve as tests of consistency or the presence of other physical effects. To remove from $K^\alpha(z)$ any dependence of $Z^\alpha_{k\ell}$ on nuclear mass, we divided in each case by the equilibrium rotational parameter B_e of CH to the appropriate power. The values of these coefficients c_j and h_j^α are presented in Table II.

TABLE II. Coefficients c_j of V(z) and h_j^α of $K^\alpha(z)$ of the radial functions of CH in the state $X\,^2\Pi_r$.

j	V(z)	A(z) /m^{-1}	γ(z) /10^{-3}	p(z) /10^{-3}	q(z) /10^{-6} m
0	(14150193 ± 77) m^{-1}	2805.119 ±0.037	−1.7883 ± 0.0020	2.418 ±0.016	1.88360 ± 0.00022
1	− 1.22310 ± 0.00020	576.77 ± 0.45	2.859 ± 0.072	-6.32 ±0.41	-7.236 ± 0.022
2	0.6218 ± 0.0011	256.66 ± 0.58	2.76 ± 0.20	3.3 ±1.2	13.782 ± 0.062
3	− 0.2202 ± 0.0040		-4.59 ±0.73	54 ± 12	14.0 ± 1.3
4	0.014 ± 0.030			-164 ± 44	9.6 ± 5.3
5	− 0.39 ± 0.15				
6	1.44 ± 0.55				

Using the known dependence of the various coefficients $Y_{k\ell}$ and $Z_{k\ell}$ on nuclear mass, we have then generated the predicted values of the band parameters of CD in the vibrational states $0 \leqslant v \leqslant 4$ of the ground electronic state which are presented in Table III. At each stage of the analysis we have estimated the standard errors of the values of all deduced coefficients and parameters;[16] such error is ultimately propagated from the uncertainty of the frequency measurements reflected in the given band parameters of CH.[7,10]

TABLE III. Band parameters/m-’ of CD in vibrational states of the electronic state X $^2\Pi_r$.[a]

Parameter	v =o	v = l	v = 2	v = 3	v = 4
T_v	0	203 145.06(37)	399458.63(58)	589005.57(79)	771840.00(99)
B_v	768.93 19(32)	747.8757(59)	726.9709(93)	706.190(12)	685.508(16)
$D_v/10^{-2}$	4.26856(44)	4.21774(58)	4.16856(79)	4.12102(99)	4.0751(13)
$H_v/10^{-6}$	1.82320(34)	1.79 130(99)	1.7547(17)	1.7 133(24)	1.6673(30)
$L_v/10^{-10}$	− 1.1822(14)	−1.1840(42)	−1.1747(70)	−1.1543(98)	−1.123(12)
A_v	2812.139(46)	2826.179(90)	2840.22(14)	2854.26(20)	2868.30(25)
$A_{Dv}/10^{-2}$	3.177(14)				
$A_H/10^{-7}$	4.89(23)				
γ_v	−1.3626(16)	−1.2997(17)	−1.2368(19)	−1.1739(22)	-1 .1 1 10(25)
$\gamma_{Dv}/10^{-4}$	1.238(30)	1.257(32)	1.276(35)	1.295(38)	1.315(43)
$\gamma_H/10^{-9}$	5.42(5 1)				
p_v	1.841(23)	1.756(27)	1.672(33)	1.588(41)	1.504(50)
$p_{Dv}/10^{-4}$	−2.44(13)	−1.90(28)	−1.36(44)	−0.82(60)	−0.28(77)
$p_{Hv}/10^{-8}$	0.52(43)	−0.50(56)	−1.54(77)	−2.56(99)	−3.6(12)
q_v	1.12943(17)	1.09908(35)	1.06873(56)	1.03838(78)	1.00803(99)
$q_{Dv}/10^{-4}$	−2.3948(74)	−2.3398(75)	−2.2848(76)	−2.2299(81)	−2.1749(87)
$q_{Hv}/10^{-8}$	2.745(19)	2.709(48)	2.674(76)	2.64(10)	2.60(14)

[a] Numbers in parentheses indicate one estimated standard error in units of the final printed digit.

III. DISCUSSION

In addition -to the tabulated values of the coefficients c_j and h_j^α we have produced figures to depict the variation of the radial function of each respective molecular property with internuclear distance. In Fig. 1 is plotted the rotationless potential energy; in the range of R near $R_e/10^{-10}$ m = 1 .1 197788 ± 1.8 x 1 0^{-6} the full line represents the function V(z), and an approximate analytic function has been plotted as a broken line to indicate qualitatively the behaviour of the potential energy at energies greater than that corresponding to the state v = 4 which is the upper limit of the available accurate spectral data.[7] Hence the classical turning points of the state v = 4, specifically $R/10^{-10}$ m = 0.87 and 1.61, represent approximately the limits of the range of validity of any other radial functions

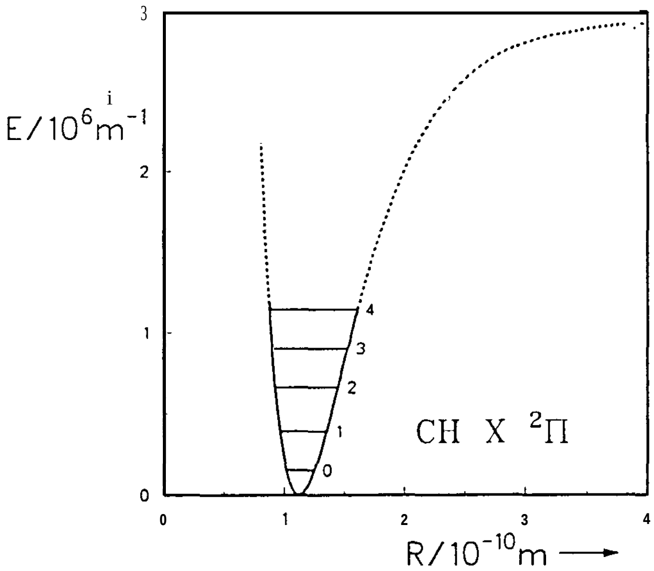

FIG. 1 The potential-energy function of CH in the ground electronic state X $^2\Pi_r$; the full line is the accurate function V(R) and the broken line is an approximate continuation of qualitatively correct shape. The horizontal lines indicate the energies of the known vibrational states.

generated from band parameters for states of CH with v $\leqslant$ 4. In Figs. 2-5 we have plotted the curves corresponding to A(R), y(R), p(R) and q(R) respectively. Note that although the spectral coefficients A,, A_{Dv}, γ_v etc. and the corresponding quantities $Z^{\alpha}_{k\ell}$ all have dimensions, specifically the SI units m^{-1} for wavenumber, the functions $\gamma(R)$ and p(R) are dimensionless, whereas the functions A(R) and q(R) bear units appropriate to their derivation. These functions provide a sensitive test of the quality of quantal computations, for instance the quality of the wavefunction in the Schrodinger procedure.

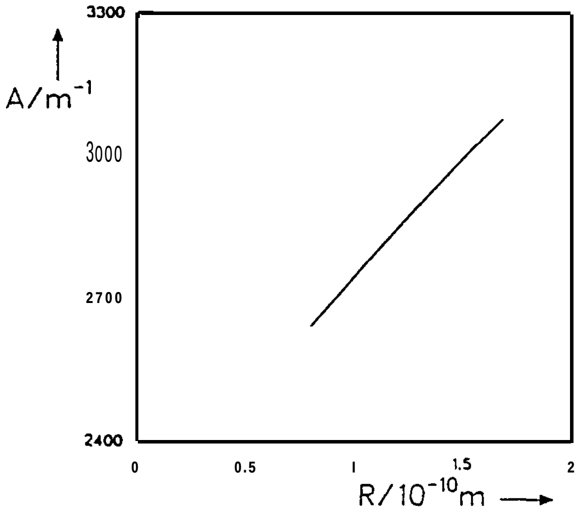

FIG. 2 The function A(R) for the spin-orbital interaction of CH in the ground electronic state X $^2\Pi_r$

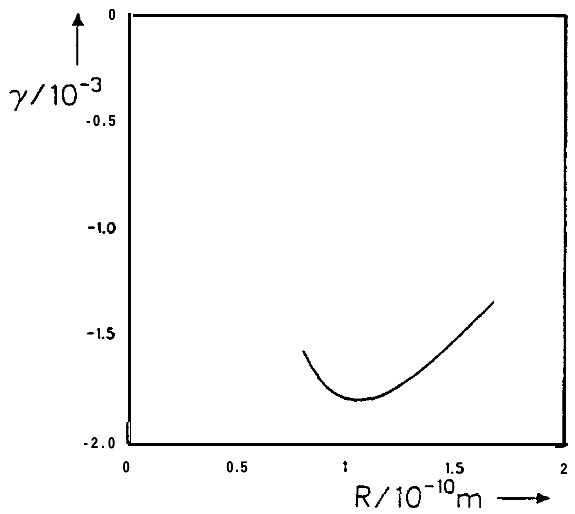

FIG. 3 The function γ(R) for the spin-rotational interaction of CH in the ground electronic state X $^2\Pi_r$.

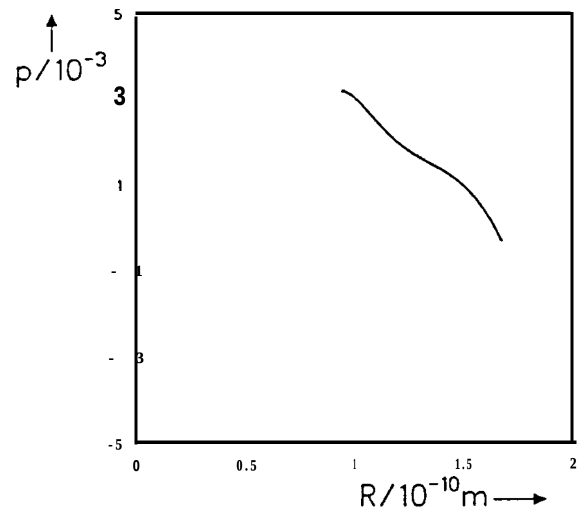

FIG. 4. The function p(R) for spin uncoupling or Λ-doubling effects of CH in the ground electronic state $X^2\Pi_r$.

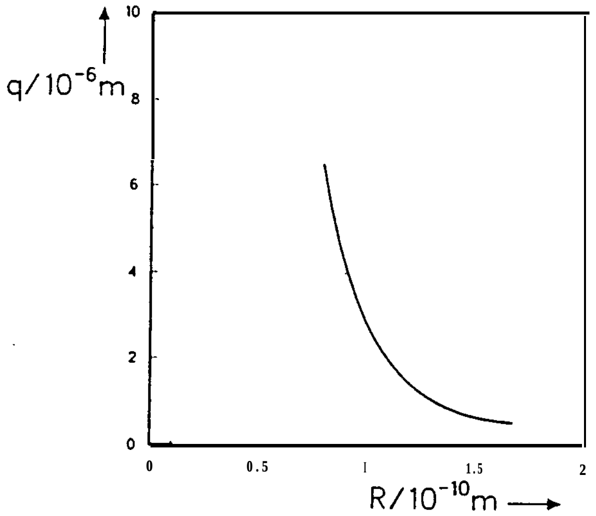

FIG. 5. The function q(R) for the orbital-rotational interaction or related Λ-doubling effects of CH in the ground electronic state $X^2\Pi_r$.

Beside the precision of each value in Table I indicated by its stated estimated standard error, one has tests of consistency because values of $Y_{k\ell}$ or $Z^{\alpha}_{k\ell}$ with $\ell>1$ are in principle fully defined by the corresponding values of $Y_{k\ell}$ or $Z^{\alpha}_{k\ell}$ with $\ell<2$. For instance the fact that the values/m^{-1} of $Y_{02} = -0.14778$, $Y_{12} = 0.002465$, $Y_{03} = 1.172 \times 10^{-5}$ and $Y_{04} = -13.91 \times 10^{-10}$ calculated from the potential-energy coefficients c_j agree closely with the corresponding fitted values in Table I (which are particularly sensitive to both error of measurement of spectral frequencies and the finite extent of the data) indicates that the derived function V(z) is an acceptably accurate representation of the adiabatic potential energy of CH. Analogously the agreement between the calculated value/m^{-1} of $Z^q_{02} = 3.27 \times 10^{-7}$ and the fitted value in Table II is satisfactory. Although the calculated value/m^{-1} of $Z^p_{02} = 0.661 \times 10^{-7}$ differs from the value 1.09×10^{-7} for v = 0 which was determined from microwave data,[17] the latter data even though of relatively great precision are of limited extent; in any case p_{Hv} for v = 0 is only an approximation to Z^p_{02}.

Comparison is also possible between the calculated values of the band parameters of CD in the state v = 0 with the experimental values which are available.” The latter data were obtained from measurements of the pure rotational transitions in the far infrared region; only transitions up to J = 6½ were measured,” a much smaller range than that in the optical spectra,[7] up to J = 23½, although the latter spectra were measured with relatively inferior resolution and frequency accuracy. For this reason the values of the spectral parameters from the pure rotational transitions would not be expected to agree exactly with those from the optical results. In fact the agreement is reasonable, in the range from a few per cent (or approximately the estimated standard errors in some cases) to twenty per cent (for unconstrained values); the stated values for the states $1 \leqslant v \leqslant 4$ of CD may consequently be expected to have similar predictive reliability. The estimates of error of all quantities reflect the wavznumber uncertainty ultimately propagated from the data of CH; apart from the approximations stated above, the error from the model, including the neglect of terms of higher order, is much smaller than the experimentally caused uncertainties.

IV. CONCLUSIONS

Based on our analysis of the spectral data of CH in the ground electronic state $X^2\Pi_r$,[7] we have not only extracted the applicable radial functions, specifically V(R), A(R), y(R), p(R) and q(R) displayed in the figures, but also predicted the band parameters of CD for the vibrational states $0 \leqslant v \leqslant 4$. The tests of consistency and with the few known data for CD are satisfactory.

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