Radial Functions of CH⁺ in the Electronic State A ${}^{1}\Pi$

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Abstract

From published data of the spectral parameters of ${}^{12}C^{1}H^{+}$ and ${}^{12}C^{2}H^{+}$ in the A ${}^{1}\Pi$ electronic state, the dependences on internuclear separation R of the internuclear potential energy, the adiabatic and non-adiabatic contributions to the molecular energy, and the interaction of the electronic orbital and rotational angular momenta have been derived, all applicable within the range $0.99 < R/10^{-10}$ m < 1.90.

Introduction

An important fundamental application of spectroscopy in relation to physical chemistry or molecular physics is the derivation of radial functions that describe how molecular properties depend on the internuclear distance R (within the Born-Oppenheimer procedure in which the motions of electrons and nuclei are treated separately). For diatomic molecules like ${}^{12}C{}^{16}O$ described as having an electronic closed shell in its ground and some electronically excited states, the resulting spectra within or between those states are relatively simple, consisting of only two branches (denoted P and R) of lines in a given band. When, however, electronic states with open shells, denoting net spin or orbital angular momentum, are involved in spectral transitions, further complications arise in the form of increased numbers of branches of spectral lines within a given band. A challenge to the chemist as spectroscopist is to convert the spectral information implied by the fact of the additional branches into radial functions that may convey some chemical meaning. In this paper I present a simple analytic procedure that is applicable to spectra involving ${}^{1}\Pi$ electronic states.

Among the chemical substances that exist as free diatomic molecules, few if any have a ground electronic state described by the term symbol ${}^{1}\Pi$ that indicates one unit of electronic orbital angular momentum but no net electronic spin angular momentum. Although such an excited state is common for a molecule with a ${}^{1}\Sigma$ (or other) ground electronic state, for this excited state there exist relatively few collections of spectral data in the form of energy coefficients. The reason is that these electronic states are beset by perturbations, specific interactions with other electronic states that result in irregularities in the transition frequencies, as well as diffuseness of lines and other hindrances to the characterization of these states in the manner of regular ground

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electronic states. On the other hand, the analysis of these perturbations¹ of ${}^{1}\Pi$ states can provide information about the existence and properties of other electronic states that are more difficultly observed directly.

The ${}^{1}\Pi$ electronic state is of interest because one may consider it to be almost the simplest, after the ${}^{1}\Sigma$ state, to describe by the conventional analytic relations for its energy terms. The specification Π implies the existence of a degenerate pair of electronic states, but the interaction of the electronic orbital angular momentum **L** with the rotational angular momentum **R** of the nuclei about the molecular centre of mass results in the removal of this degeneracy. To form the Hamiltonian for the ${}^{1}\Pi$ state, one must add to the effective potential energy of a rotating molecule (with quantum number J for the total angular momentum) of a molecule in a ${}^{1}\Sigma$ state

$$V_{\rm eff} = V(R) + B_{\rm e} R_{\rm e}^2 J(J+1)/R^2$$

a further term,² proportional to L.R, to take account of this coupling of angular momenta; here R and R_e in the centrifugal term represent the instantaneous and equilibrium internuclear separations respectively. Then the energy terms within the ${}^{1}\Pi$ state are expressed by the formula³

$$E(v, J) = G(v) + B_v[J(J+1)-1] - D_v[J(J+1)-1]^2 + \dots$$
$$\pm \frac{1}{2}[q_v + q_{Dv}J(J+1)][J(J+1)]$$

in which the coefficient q_v is a measure of the rotationally induced splitting or Λ doubling of the Π electronic state, and the q_{Dv} coefficient takes account of any further rotational dependence of the Λ doubling; G(v) represents the purely vibrational energy, whereas B_v and D_v are the inertial and centrifugal-distortion parameters respectively.

One of the few species having a ${}^{1}\Pi$ state for which fairly precise spectral data exist³ is ${}^{12}C^{1}H^{+}$; not only are there data over a moderate range of values of the vibrational ($0 \le v' \le 3$) and rotational ($0 \le \Re \le 13$) quantum numbers, but also data are available⁴ over similar ranges for the isotopically substituted species ${}^{12}C^{2}H^{+}$. Although, in common with other typical ${}^{1}\Pi$ states, the A state of this species shows the effects of perturbations attributed to interactions with nearby electronic states, nevertheless the data are of sufficient extent and quality that their further analysis to yield fundamental molecular properties may be practicable. In previous work,⁵ I demonstrated how such spectral data, the parameters from the analysis of the wavenumbers of transitions having both a vibrational and rotational variation, could be treated by means of a quantitative analytic formulation so as to yield the values of not only the coefficients that indicate the radial dependence of the adiabatic and non-adiabatic effects; the theory was there applied⁵ only to instances of compounds

⁴ Bembenek, Z., Cisak, H., and Kepa, R., J. Phys. B: At. Mol. Phys., 1987, 20, 6197.

¹ Lefebvre-Brion, H., and Field, R. W., 'Perturbations in the Spectra of Diatomic Molecules' (Academic Press: Sydney 1986).

² Steinfeld, J. I., 'Molecules and Radiation' (M.I.T. Press: London 1985).

³ Carrington, A., and Ramsay, D. A., Phys. Scr., 1982, 25, 272.

⁵ Ogilvie, J. F., Chem. Phys. Lett., 1987, 140, 506.

with molecular ${}^{1}\Sigma$ ground electronic states. In this work, I analogously demonstrate both how this approach can be simply extended to an electronically excited state having net orbital angular momentum, and that a similar treatment can yield the radial dependence of the interaction of the orbital and rotational angular momenta.

Calculations and Results

The essential relation that expresses the energy of the vibration-rotational states within a particular ${}^{1}\Pi$ electronic state is

$$E(v, J) = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} (Y_{kl} + Z_{kl})(v + \frac{1}{2})^{k} [J(J+1) - 1]^{l}$$

Here the Y_{kl} coefficients take account of the effects of the internuclear potential energy and the adiabatic (from the finite mass of the nuclei) and the non-adiabatic (from the interactions with other electronic states) corrections to it. The Z_{kl} coefficients in this equation take account of the extra branches of lines in the spectrum beyond those that would appear for transitions involving only ${}^{1}\Sigma$ electronic states. Specifically in the case of ${}^{1}\Pi$ states, the Z_{kl}^{q} coefficients take account of the A-doubling effects; in particular, the terms involving the coefficients G(v), B_v , D_v ... in the previous equation are related⁶ to the Y_{kl} coefficients, and the coefficients q_v, q_{Dv} ... lead to the Z_{kl}^q coefficients in exactly the same way. The Z_{kl}^a coefficients are also used⁵ to take account of the adiabatic and non-adiabatic corrections, because there is a common relationship between both the sets of Z_{kl} coefficients and the parameters in the radial functions to be defined. First we consider the information about non-mechanical effects (adiabatic, non-adiabatic, and any other having the same mass dependence, as opposed to the mechanical effects of the nuclear vibration and rotation about the centre of mass) that can be deduced from the combination of the data for ${}^{12}C^{1}H^{+}$ and ${}^{12}C^2H^+$. Thus we write the coefficients Y_{kl}^i of each isotopic species in the form⁵ that discloses an inherent mass dependence:

$$Y_{kl}^{i} = U_{kl} \mu_{i}^{-(k+2l)/2} [1 + m_{e} (\Delta_{kl}^{a} / M_{a} + \Delta_{kl}^{b} / M_{b})]$$

Here $\mu_i = M_a M_b/(M_a + M_b - m_e)$ is the reduced mass⁷ of the net singly charged molecular cation having masses M_a and M_b of the separate neutral atoms, and m_e is the electronic (rest) mass. In the case of the present species ${}^{12}C^{1}H^{+}$ and ${}^{12}C^{2}H^{+}$, because of the lack of appropriate spectral information for isotopic species containing other than carbon-12, the parameters U_{kl} , not being formally independent of mass due to the incorporation of the unknown effects of the carbon atoms, become designated U'_{kl} . The resulting necessarily simplified formula is

$$Y_{kl} = U'_{kl} \mu_i^{-(k+2l)/2} [1 + m_e \Delta^{\rm H}_{kl} / M_{\rm H}]$$

The available information^{3,4} on differences of vibrational energy in the A ¹ Π state of both ¹²C¹H⁺ and ¹²C²H⁺ was fitted to Lagrangian polynomials, in the absence of sufficient data to permit statistical methods; the resulting values of the coefficients are listed in Table 1. Then the further fitting to the above equation yielded the two

⁶ Dunham, J. L., Phys. Rev., 1932, 41, 721.

⁷ Watson, J. K. G., J. Mol. Spectrosc., 1980, 80, 411.

pairs of values of the parameters $U'_{k,0}$ and $\Delta^{\rm H}_{k,0}$, k = 1, 2. Because the data for the rotational dependences are slightly more abundant, statistical methods (weighted polynomial regression⁸ with appropriate tests of significance) were employed to extract the parameters so as to fit best the available data. These results are also listed in Table 1.

Table 1.	Basic dat	ta for	the A	$^{1}\Pi$ state	of	${}^{12}C^{1}H^{+}$	and	${}^{12}C^{2}H^{+}$	derived	from	published
				spectra	l ps	arameters	3,4				

k	l	¹² C ¹ H ⁺	${}^{12}C^{2}H^{+}$
		Y_{kl}/m^{-1}	
1	0	$186441 \cdot 417 \pm 0 \cdot 13$	136738.44 ± 1.2
2	0	-11585.2	-6087.5
3	0	263.45	78.66
0	1	1190.19 ± 0.31	$641 \cdot 598 \pm 0 \cdot 091$
1	1	-95.915 ± 0.40	-37.448 ± 0.047
2	1	0.5214 ± 0.10	· ·
0	2	$-0.19029 \pm 1.3 \times 10^{-4}$	$-0.056238 \pm 1.7 \times 10^{-5}$
1	2	$-0.013644 \pm 1.6 \times 10^{-4}$	$-0.0022994 \pm 2.4 \times 10^{-5}$
2	2	$0.002044 \pm 4.1 \times 10^{-6}$	$0.0001830 \pm 6.6 \times 10^{-6}$
		Z_{kl}^q/m^{-1}	
0	0	4.07235 ± 0.00033	1.2193 ± 0.0075
1	0	-0.2984 ± 0.0049	-0.1009 ± 0.013
2	0	-0.00634 ± 0.0014	0.00726 ± 0.0036
0	1	$(-1.59\pm0.20)\times10^{-3}$	$(-5.74\pm0.96)\times10^{-4}$
1	1	$(-0.46\pm0.25)\times10^{-3}$	$(2.75\pm1.58)\times10^{-4}$
2	1	$(+0.144\pm0.067)\times10^{-3}$	$(-0.58\pm0.46)\times10^{-4}$
		U'_{kl}	$\Delta_{kl}^{\mathbf{H}}$
1	0	$179375 \cdot 0 \pm 1 \cdot 3$	4.110 ± 0.019
2	0	- 10230	98
0	1	1106.52 ± 0.87	0.16312 ± 0.00012
1	1	-83.65 ± 1.1	51.45 ± 22

Each stated uncertainty	indicates o	one estimated	standard	error
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Through the values of the parameters Δ_{kl}^{H} generated above, the relation

$$Z_{kl}^{a} = U_{kl}^{\prime} \mu^{-(k+2l)/2} m_{e} \Delta_{kl}^{H} / M_{H} - Y_{kl}^{(2)}$$

was used to transform the data into the standard form;⁵ the second-order mechanical contribution $Y_{kl}^{(2)}$ was neglected for both $Z_{1,1}^{a}$ and $Z_{2,0}^{a}$ because of the lack of values of some necessary coefficients defining the potential-energy function, but the magnitude of these corrections would in any case be much smaller than the relatively large values of these Z_{kl}^{a} quantities. From the resulting values of the parameters U'_{kl} , Z_{kl}^{a} and Y_{kl} (in the cases for which the required U'_{kl} values were indeterminate), the radial functions for potential energy and the adiabatic and non-adiabatic corrections were determined. As previously,⁵ the radial functions were based on the superior variable⁹ $z = 2(R - R_{e})/(R + R_{e})$ for reduced internuclear displacement, in the following

⁸ Ogilvie, J. F., and Abu-Elgheit, M. A., Comput. Chem., 1981, 5, 33.

⁹ Ogilvie, J. F., Proc. R. Soc. London, Ser. A, 1981, 378, 287; 1982, 381, 479.

functional forms:

$$V(z) = c_0 z^2 \left(1 + \sum_{j=1}^{\infty} c_j z^j \right) \qquad K^{a}(z) = \sum_{j=1}^{\infty} h_j^{a} z^j$$

Then the relations for the quantities U'_{kl} and Y_{kl} ,¹⁰ and Z_{kl} ,⁵ in terms of the coefficients c_j , h_j , and the expansion parameter $\gamma = 2B_e/\omega_e$ were directly applied in order to produce the desired results, listed in Table 2.

Table 2. Values of the derived coefficients c_j , h_j^a and h_j^q for the radial functions describing the internuclear potential energy V(z), adiabatic and non-adiabatic effects $K^a(z)$, and the interaction $K^q(z)$ of the electronic orbital and rotational angular momenta in the A ¹II state of ¹²C¹H⁺ and ¹²C²H⁺

j	C;	h_{1}^{a}/m^{-1}
0	$(7269525 \pm 11800) \text{ m}^{-1}$	_ /
1	-2.04246 ± 0.0044	-1968.09 ± 0.23
2	1.5958 ± 0.017	29570 ± 75
3	1.0121 ± 0.097	$(-5.02\pm0.18)\times10^{5}$
4	-1.621 ± 0.19	3.6×10 ⁵
	$h_{i}^{q}/10^{-6}$	m
	¹² C ¹ H ⁺	¹² C ² H ⁺
0	2.8649 ± 0.0022	2.9930 ± 0.018
1	-6.8845 ± 0.86	-15.8 ± 2.7
2	11.47 ± 3.5	$38 \cdot 18 \pm 10 \cdot 7$
3	-63.78 ± 7.9	205 ± 155
4	287 ± 87	1444 ± 945
5	-492 ± 302	2412 ± 1300

In order to treat the data for the Λ -doubling parameters q_v and q_{Dv} , in a preliminary step the available values^{3,4} for ${}^{12}C^{1}H^{+}$ and ${}^{12}C^{2}H^{+}$ were separately fitted to polynomials in the vibrational functional $(v + \frac{1}{2})$; the resulting coefficients are then readily identified as $Z_{k,0}^{q}$ and $Z_{k,1}^{q}$ respectively. Explicitly

$$q_v = \sum_{k=0}^2 Z_{k,0} (v + \frac{1}{2})^k \qquad q_{Dv} = \sum_{k=0}^2 Z_{k,1} (v + \frac{1}{2})^k$$

Both sets of the latter values were then directly fitted to the extant relations^{5,11,12} for Z_{kl} in order to yield for each separate species the values of the coefficients h_j^q defining the radial dependence of the interaction of the electronic orbital and rotational angular momenta according to the relation

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

In this case a factor B_e^2 was included in each expression for Z_{kl}^q , in order to bestow the proper mass dependence;¹³ for this reason also, the resulting values of the parameters h_i^q have the dimensions of length.

- ¹⁰ Ogilvie, J. F., Comput. Phys. Commun., 1983, 30, 101.
- ¹¹ Ogilvie, J. F., J. Mol. Spectrosc., 1988, 128, 216.
- ¹² Ogilvie, J. F., J. Phys. B: At. Mol. Phys., 1988, 21, 1663.
- ¹³ Gordy, W., and Cook, R. L., 'Microwave Molecular Spectra' (John Wiley: New York 1985).

Discussion

The interactions between electronic states that are responsible (according to the classical interpretation) through the rotational effect for the Λ doubling are of a similar nature to those resulting in irregularities in the wavenumbers of the lines denoting the spectral transitions. Therefore, as remarked previously,^{3,4} there is some difficulty in fitting satisfactorily both the vibrational intervals and the rotational parameters of both ${}^{12}C^{1}H^{+}$ and ${}^{12}C^{2}H^{+}$ to the conventional expansions in $(v+\frac{1}{2})$ as power series; consequently the fitted parameters lack physical significance to some extent. However, although the values of these parameters fail to reproduce the wavenumbers of the spectral lines within their precision of measurement, the differences are sufficiently small as to indicate that some measure of physical meaning does remain. The basis of the present treatment rests on this condition. Furthermore, the proximity to the A ${}^{1}\Pi$ state of other electronically excited states, 14 especially the a and other ${}^{3}\Pi$ states and other molecular states correlating with the same dissociation products (C^{+ 2}P and H²S), provides a qualitative explanation of the relatively large magnitudes of the parameters $\Delta_{kl}^{\rm H}$, except for $\Delta_{0,1}^{\rm H}$, and of the correspondingly comparatively large magnitudes⁵ of the resulting coefficients h_{j}^{a} , j > 1, although the fitting difficulties described above could also contribute to the large magnitudes. The radial function $K^{a}(z)$ for the adiabatic and non-adiabatic effects contains no constant term h_{0}^{a} because the measure of these effects is by definition relative to what exists at the equilibrium internuclear separation R_e , at which z = 0.

v	q_v/r	n^{-1}	$q_{Dv}/10^{-4} \text{ m}^{-1}$			
	Obs.	Calc.	Obs.	Calc.		
0	1.1703 ± 0.0049	1.1494 ± 0.0034	-4.45 ± 0.41	-2.73 ± 0.28		
1	1.0885 ± 0.0094	1.0837 ± 0.0063	-3.32 ± 0.67	-3.02 ± 0.50		
2	1.0080 ± 0.0095	1.0160 ± 0.0090	-1.84 ± 0.87	-3.06 ± 0.81		
3	0.959 ± 0.016	0.9462 ± 0.013	-3.9 ± 1.5	-2.86 ± 1.1		

Table 3. Values of the Λ -doubling parameters q_v and q_{Dv} for ${}^{12}C^2H^+$, observed⁴ and calculated from the spectral data³ of ${}^{12}C^1H^+$

The present work marks the first determination of the radial dependence of the interaction of the electronic orbital and rotational angular momenta of a ${}^{1}\Pi$ state according to an analytic procedure like that outlined above. In the diagram¹⁴ summarizing the results of various calculations of the potential-energy curves of various electronic states of CH⁺, the A ${}^{1}\Pi$ state is depicted as a single curve for the rotationless potential energy. Because of the interactions with the other states depicted, ¹⁴ the degeneracy is removed so that two distinct curves should exist when the centifugal term is taken into account; then the function $K^{q}(z)$ here derived from the published spectral parameters is related to the difference between those two curves for a given value of the quantum number J > 1.

We may compare the values of the derived coefficients h_j^q in Table 2 for ${}^{12}C^1H^+$ and ${}^{12}C^2H^+$. Although the values of h_o^q for the two species are in small but significant disagreement, the other values h_j^q , j > 0, seem to disagree markedly. To locate the origin of the discrepancies, I used all the values of h_j^q calculated from the spectral

¹⁴ Cosby, P. C., Helm, H., and Moseley, J. T., Astrophys. J., 1980, 235, 52.

data³ of only ¹²C¹H⁺ to predict the values of q_v and q_{Dv} of ¹²C²H⁺. The observed⁴ and calculated values, with their accompanying standard errors, are compared in Table 3. One can see that these sets of q_v , apart from q_0 curiously (which is also consistent with the disagreement in the values of h_0^q), agree reasonably closely; the differences in the two sets of q_{Dv} are greater but the uncertainties in the values are relatively large. Bembenek *et al.* have already shown⁴ the great range of values of these spectral parameters q_v and q_{Dv} from various experimental spectra of ¹²C²H⁺. It seems necessary to conclude that, because of the small magnitudes of the coefficients, q_{Dv} in particular, and because of the limited range of rotational quantum number \Re of the measured lines that enabled the estimation of the value of the latter parameters, these values are especially sensitive to effects of spectral resolution, finite linewidth, and the consequent errors of measurement, not to forget the effects of pertubations on these ¹\Pi states.

Anyhow, by means of the available spectral data^{3,4} and the present analytic procedure, one can predict values of $Z_{0,2}^q$ to be approx. $1 \cdot 6 \times 10^{-7} \text{ m}^{-1}$ for ${}^{12}\text{C}^1\text{H}^+$ and $6 \cdot 8 \times 10^{-8}$ or $1 \cdot 3 \times 10^{-8} \text{ m}^{-1}$ for ${}^{12}\text{C}^2\text{H}^+$; the last value is predicted on the basis of the data for ${}^{12}\text{C}^1\text{H}^+$. These values are approximately those expected for the coefficients q_{DDv} of $[J(J+1)]^2$ in the power series for the splitting of the Λ doublets that has q_{Dv} as the coefficient of J(J+1). Finally, all the derived radial functions should be valid in the region between the classical vibrational turning points of the state $\Lambda^{1}\Pi$, v' = 3 of ${}^{12}\text{C}^{1}\text{H}^+$, specifically $0.99 < R/10^{-10} \text{ m} < 1.90$.

Conclusions

From the published spectral data for the rovibronic transition A ${}^{1}\Pi$ -X ${}^{1}\Sigma^{+}$ of the molecular cationic species ${}^{12}C^{1}H^{+}$ and ${}^{12}C^{2}H^{+}$, I have derived the dependence on internuclear separation R of the internuclear potential energy V(z), the adiabatic and non-adiabatic effects $K^{a}(z)$, and the interaction $K^{q}(z)$ between the electronic orbital and rotational angular momenta for the A ${}^{1}\Pi$ electronic state.

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