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A comparison of approaches for reduction of vibration-rotational spectra of NaCl $X\ ^1\Sigma^+$ to parameters of radial functions

J.F. Ogilvie [1], Marcin Molski *

Department of Theoretical Chemistry, Faculty of Chemistry, Adam Mickiewicz University, ul. Grunwaldzka 6,
PL 60-780 Poznań, Poland

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Abstract

We compare applications of a deformationally self-consistent procedure and of hypervirial perturbation theory, as embodied in a computer programme Radiatom, to spectral data of ^{23}Na^{35}Cl and ^{23}Na^{37}Cl in the electronic ground state $X\ ^1\Sigma^+$comprising 1210 vibration–rotational transitions. From a marginally evaluated value of a parameter related to nonadiabatic rotational effects we predict rough values of electric dipolar moment and rotational g-factor; the former is near a known experimental value. Comparison is also made with values transformed from results obtained with a potential-energy function of exponential form. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Diatomic molecules of a particular chemical compound in the gaseous phase can produce spectral lines in microwave and infrared regions, in absorption or emission, that number in the thousands. During the past decade methods have been developed that enable data in the form of frequencies or wavenumbers characterising these many transitions, associated with rotational and vibrational molecular motions, to be reproduced precisely for all isotopic variants with few parameters [1]. Data reduction to this extent involves evaluation of radial functions that have theoretical significance. If one employs merely empirical coefficients in power series with quantum numbers J for rotation and v for vibration, the parameters required for each isotopic variant might number similarly to, or even appreciably greater than, parameters for various radial functions from data of multiple isotopic variants. A concurrent fit of data of all isotopic species is evidently a more efficient process than separate fits of individual isotopic variants. In some cases

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* Corresponding author. Tel.: +48-61-869-9181-492; fax: +48-61-865-8008.

E-mail address: marcin@rovib.amu.edu.pl (M. Molski)

[1] Present address: Centre for Experimental and Constructive Mathematics, Simon Fraser University, Burnaby, BC V5A 1S6, Canada. E-mail: ogilvie@cecm.sfu.ca

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moreover, a combined fit has been demonstrated to yield information about electric and magnetic molecular properties even though a data set comprises transitions for samples measured in the absence of externally applied electric or magnetic field. For instance, a fit of global data of GeS enabled prediction of both the equilibrium electric dipolar moment and the rotational g-factor with values near those defined by experiment [2]. For GaH for which an experimental value of neither quantity is available, from only vibration–rotational transitions an electric moment was poorly evaluable but a rotational g-factor $g_J = -3.22 \pm 0.10$ [3], for $^{69}Ga^1H$ agreed closely with subsequently reported values calculated in the range $[-3.45, -2.94]$ depending on the level of approximation with a perturbative polarisation propagator [4]. In contrast, from an alternative fit of the same spectral data with fewer adjustable parameters a later prediction $g_J = -4.2544 \pm 0.0046$ agreed poorly with preceding values [5]. Because measurements of the Zeeman effect to yield accurate values of g_J are seldom performed at present, such information from other experiments might prove a useful addition to the chemical literature, to serve as tests of quantum-chemical calculations more sensitive than electric dipolar moment for example.

Various authors employ particular algorithms to reduce spectral data and to express results therefrom in parameters in disparate sets. Even when a variable that serves as argument of radial functions is common, parameters that occur as coefficients of that argument to various powers might assume widely disparate values. If one seeks to attach theoretical significance to radial functions, the apparent variability of values pertaining to the same chemical species deters their application in other contexts. In the present work we compare applications of two computer programmes Radiatom [6], and DS-cP [5], to data of NaCl for which available spectra of satisfactory quality involve vibrational states up to $v = 8$ and rotational states up to $J = 118$ [7]. A programme DS-cP, signifying a deformationally self-consistent procedure, employs analytic expressions for a purely vibrational contribution to molecular eigenenergies but relies on a numeric algorithm to take account of rotational and other contributions [5]. Because such a numeric treatment inherently lacks explicit analytic expressions to prove its consistency with standard convention, it is essential to verify that this algorithm provides in practice rotational energies that conform to those from an established formalism. In contrast a programme Radiatom is based on an analytic formalism originated by Dunham [8], but with treatment greatly extended to include adiabatic and nonadiabatic effects [6]. For purpose of comparison the data of NaCl in the present set [7], are especially useful because the total purely rotational energy associated with any vibrational state is as great as the purely vibrational energy for the highest vibrational state to which transitions are recorded.

In this report we outline our algorithms embodied in two computer programmes and describe their application to data of NaCl as a basis of comparison of underlying approaches.

2. Methods

2.1. Algorithm in Radiatom

The algorithm in Radiatom is based on results from hypervirial perturbation theory [9], that enables efficient generation of analytic expressions for energies of vibration–rotational states of a diatomic molecule suitable for fitting precise spectral data. We outline here the salient features of this algorithm.

The effective potential energy consists of internuclear potential energy $V(R)$, implemented in Dunham's form [8], and rotational kinetic energy:

$$V_{\text{eff}}(R) = V(R) + B_e R_e^2 J(J+1)/R^2 \tag{1}$$

or explicitly:

$$V_{\text{eff}}(R) = a_0 x^2\left(1 + \sum_{j=1} a_j x^j\right) + B_e J(J+1)\left(\sum_{j=1} (-1)^j (j+1) x^j\right) \tag{2}$$

in which, according to spectral tradition, we adopt units of wavenumber for pertinent quantities. The reduced displacement coordinate x is defined as $(R-R_e)/R_e$ in which R is the instantaneous internuclear separation and R_e is the equilibrium separation, i.e. the internuclear distance for which potential energy is a minimum for the rotationless state with $J=0$ [8]. The operator of internuclear kinetic energy, along the internuclear vector, is included in its standard form $\hat{p}^2/(2\mu)$ in which the reduced atomic mass $\mu = M_aM_b/(M_a + M_b)$. A temporally independent equation of Schrodinger's form is solved as an eigenvalue problem with one degree of freedom according to the method based on hypervirial perturbation theory [9], to yield eigenvalues:

$$E_{vJ} = \sum_{k=0}\sum_{l=0} Y_{kl}(v+1/2)^k[J(J+1)]^l \tag{3}$$

Details and justification of this method are presented elsewhere [9]. Analytic expressions of term coefficients Y_{kl} obtained with this means are identical to those that Dunham [8], obtained originally by manual application of the quasi-classical method of Brillouin, Kramers and Wentzel [8], and to those expressions from slightly altered methods [10,11], from alternative methods based on conventional Rayleigh–Schrodinger perturbation theory [12], and from matrix mechanics [13]; these results are all derived and verified with computer algebra [14].

To take into account the fact that a diatomic molecule is not simply a rotating oscillator composed of two structureless (point) masses but that electrons follow imperfectly one or other nucleus in its vibration and rotation about the centre of molecular mass, we extend the Hamiltonian by adding three terms to produce a form [15]:

$$\hat{H} = [1+\beta(R)]\hat{p}^2/(2\mu hc) + V(R) + V'(R) + [1+\alpha(R)]B_eR_e^2J(J+1)/R^2 \tag{4}$$

in which $V'(R)$ takes into account adiabatic effects, according to which internuclear potential energy depends not only on the distance between the nuclei but also on their relative momenta; radial functions $\beta(R)$ and $\alpha(R)$ represent nonadiabatic vibrational, and rotational effects, respectively, formally associated with interactions of the electronic state of interest, generally the electronic ground state, with electronically excited states induced by vibrational and rotational motions of the nuclei. As a result of these further terms in the Hamiltonian, additional term coefficients Z_{kl} occur in eigenvalues [16]:

$$E_{vJ} = \sum_{k=0}\sum_{l=0}(Y_{kl} + Z^a_{kl} + Z^b_{kl})(v+1/2)^k[J(J+1)]^l \tag{5}$$

In an alternative expression for eigenvalues [17]:

$$E_{vJ} = \sum_{k=0}\sum_{l=0} U_{kl}[1 + m_e(\Delta^{\mathrm{Na}}_{kl}/M_{\mathrm{Na}} + \Delta^{\mathrm{Cl}}_{kl}/M_{\mathrm{Cl}})] \tag{6}$$

coefficients $\Delta^{a,b}_{kl}$ are empirically fitted whereas coefficients U_{kl} have meaning well defined in terms of leading contributions to Y_{kl}.

We employ, instead of x in Dunham's treatment [8], a variable $z \equiv 2(R-R_e)/(R+R_e)$ for reduced internuclear displacement because of its superior properties [18,19]. The radial functions become accordingly [6]:

$$V(z) = c_0z^2\left(1 + \sum_{j=1} c_jz^j\right) \tag{7}$$

$$V'(z) = (m_e/M_a)\sum_{j=1} u^a_jz^j + (m_e/M_b)\sum_{j=1} u^b_jz^j \tag{8}$$

$$\alpha(z) = (m_e/M_a)\sum_{j=0} t^a_jz^j + (m_e/M_b)\sum_{j=0} t^b_jz^j \tag{9}$$

$$\beta(z) = (m_e/M_a)\sum_{j=0} s^a_jz^j + (m_e/M_b)\sum_{j=0} s^b_jz^j \tag{10}$$

of which only coefficients c_j with $j>0$, instead of a_j in Dunham's function $V(R)$, occur in Y_{kl}, with $U_{1,0}$ and $U_{0,1}$ and reduced atomic mass, μ; $c_0 = U^2_{1,0}/(4U_{0,1})$.

Perturbation theory is employed to produce analytic expressions for Z_{kl} [16,20], when directly produced, these expressions contain coefficients a_j and other coefficients of x that are readily converted to coefficients of z instead. Thus these expressions Z_{kl} coded in FORTRAN within Radiatom contain, in general, parameters $U_{1,0}$, $U_{0,1}$, c_j with $j>0$, s_j,t_j and u_j with the reduced atomic mass and either M$_a$ or M_b. For a particular value j for c_j, according to a model being tested to fit spectral data, only Y_{kl} that contain c_j up to that value of j in their leading terms are included in Eq. (5) for E_{vj}. In fitting spectral data with this programme parameters in a selected set with a non-linear dependence on atomic masses and vibrational and rotational quantum numbers are adjusted to yield the minimum value of a sum of squares of weighted residuals; for each transition a weight applied to the corresponding residual is the squared reciprocal of an uncertainty assigned during measurement of the wavenumber (or frequency) of that transition. The maximum value of the F-statistic is employed as a criterion to select an optimal set of parameters [6].

2.2. Deformationally self-consistent procedure

According to this numeric approach displacements of nuclei in a rotating and vibrating molecule take place in the vicinity of a dynamical equilibrium distance R_J and not $R_e \equiv R_{J=0}$ because centrifugal force exerts a deformational action [21]. If a molecule is endowed with a potential-energy function:

$$V_J(R) = \frac{\hbar^2 J(J+1)[1+\alpha(R)]}{2\mu R^2} + V(R) + V'(R) \tag{11}$$

the quantity R_J is calculated [5], according to a criterion for a minimum:

$$\left(\frac{\mathrm{d}V_J(R)}{\mathrm{d}R}\right)_{R=R_J} = \left(\frac{\mathrm{d}V_J(x)}{\mathrm{d}x}\right)_{x=x_J} = 0, \tag{12}$$

in which

$$x = (R - R_0)/R_0 \qquad x_J = (R_J - R_0)/R_0. \tag{13}$$

Having calculated R_J we expand $V_J(R)$:

$$V_J(\eta) = \sum_{j=0} b_j^J \eta^j, \tag{14}$$

$$b_j^J = (j!)^{-1}\left(\frac{\mathrm{d}^j V_J(\eta)}{\mathrm{d}\eta^j}\right)_{\eta=0} = (j!)^{-1}\left(\frac{\mathrm{d}^j V_J(x)}{\mathrm{d}x^j}\right)_{x=x_J}\left(\frac{R_0}{R_J}\right)^j \tag{15}$$

into a series with a variable, η analogous to Dunham's x [8], as an argument dependent upon J,

$$\eta = (R - R_J)/R_J \tag{16}$$

Employing Eq. (12) we remove the linear term $b_1^J\eta$ to achieve an equation of Schrodinger's form [5]:

$$\left[-B_J\frac{\mathrm{d}^2}{\mathrm{d}\eta^2} + a_0^J\eta^2\left(1 + \sum_{j=1} a_k^J\eta^j\right) - (E_{vJ} - b_0^J)\right] \psi_{vJ}(\eta) = 0, \tag{17}$$

$$a_0^J = b_2^J, \qquad a_{j>0}^J = b_{j+2}^J/a_0^J,$$

$$B_J = \hbar^2/[2\mu(R_J)^2], \tag{18}$$

that is amenable to treatment [22], according to Dunham's quasi-classical scheme [8]. The eigenvalues have a form:

$$E_{vJ} = b_0^J + \sum_{k=0} Y_{k,0}(R_J,a_j^J)(v+1/2)^k, \tag{19}$$

and $Y_{k,0}(R_J,a_j^J)$ are Dunham's purely vibrational coefficients, in analytic expressions obtained elsewhere [8], into which substitutions $\{R_0,a_j\} \rightarrow \{R_J,a_j^J\}$ are made numerically. As eigenvalues (Eq. (19)) contain unknown parameters R_J defined according to Eq. (12) for equilibrium we fit spectral data in an iterative manner [5]. For initial values of potential-energy parameters $q_j = (R_0,c_i,t_i^{a,b},u_i^{a,b})$ the roots $x_J = (R_J - R_0)/R_0$ of Eq. (12) are calculated with a bisection algorithm for each rotational state. After substitution of x_J into $E_{vJ}(x_J,q_j)$ we fit parameters q_j to experimental data using a weighted non-linear least-square routine with weights taken as inverse squares of uncertainties of experimental data. Parameters q_j evaluated in the preceding step are reintroduced into Eq. (12) enabling evaluation of further quantities x_J employed to calculate corresponding values of q_j. In the present work the singular-value decomposition method was employed to solve the normal equations, replacing the Gauss–Jordan routine without pivoting used previously, although tests indicated negligible differences between results obtained in either way.

This iterative procedure has continued to obtain the best fit according to the following criteria, the minimum number of fitted parameters N consistent with a minimum value of normalised standard deviation $\hat{\sigma} \approx 1$, a maximum value of F-statistic, and optimal values of estimated standard error σ_i of each fitted parameter i and of correlation coefficient $cc(i,j)$ between parameters i and j.

3. Data

Data reduced according to these two approaches are collected from sources specified in Table 1, which indicates also the distribution of transitions, 946 for $^{23}Na^{35}Cl$ and 264 for $^{23}Na^{37}Cl$, within specified vibrational states for pure rotational transitions and between specified vibrational states with $\Delta v = 1$ for vibration–rotational transitions. The maximum relative precision $\delta\hat{v}/\hat{v}$ of measurements within each set is also indicated there; to facilitate comparisons the published uncertainty of each transition employed in fitting parameters is the same as that adopted by Ram et al. [7].

4. Results

Application of programme DS-cP from the deformationally self-consistent procedure and of programme Radiatom to 1210 input data specified in Table 1 yields results presented in Table 2, in which an uncertainty associated with each parameter denotes one estimated standard error. No parameter of type s_j or u_j pertaining to nonadiabatic vibrational or adiabatic effects [6], was evaluable. Included in this table are other indicators of goodness of fit, the normalised standard deviation $\hat{\sigma}$ and the F-statistic.

Table 1
Rotational and vibration–rotational transitions of NaCl[a]

$^{23}Na^{35}Cl$				
States	Number of transitions	J_{max}	Maximum precision	Source
$v=0$	9	24	3×10^{-7}	a, b
$v=1$	5	24	3×10^{-7}	a, b
$v=2$	2	15	3×10^{-7}	a, b
$v=3$	1	2	3×10^{-6}	a
$v'\rightarrow v''$				
1 0	160	118	6×10^{-6}	c
2 1	153	117	6×10^{-6}	c
3 2	146	117	6×10^{-6}	c
4 3	133	117	6×10^{-6}	c
5 4	116	106	6×10^{-6}	c
6 5	101	117	10^{-5}	c
7 6	66	82	10^{-5}	c
8 7	54	75	10^{-5}	c
$^{23}Na^{37}Cl$				
$v=0$	4	17	3×10^{-7}	a, b
$v=1$	4	15	3×10^{-7}	a, b
$v=2$	1	2	3×10^{-6}	a
$v'\rightarrow v''$				
1 0	106	96	10^{-5}	c
2 1	96	91	10^{-5}	c
3 2	53	84	10^{-5}	c

[a] a, [30]; b, [31]; c, [7].

Table 2
Parameters from fits of vibration–rotational spectra of NaCl

	DS-cP	Radiatom	a^a
$U_{1,0}/\mathrm{u}^{1/2}\ \mathrm{m}^{-1}$		$135\,820.977 \pm 0.090$	147577.06
$U_{0,1}/\mathrm{u\ m}^{-1}$		302.47339 ± 0.00186	302.46813
c_0/m^{-1}	$15\,247\,100 \pm 101$	$15\,246\,877 \pm 74$	$18\,001\,062$
c_1	-2.076514 ± 0.000050	-2.076602 ± 0.000051	-2.076644
c_2	2.53322 ± 0.00024	2.54061 ± 0.00034	2.53739
c_3	-1.8344 ± 0.0039	-1.8583 ± 0.0022	-1.8528
c_4	0.3417 ± 0.0159	-0.2541 ± 0.0196	0.1087
t_0^{Cl}	-1.43 ± 0.41	-1.11 ± 0.39	
$k_e/N\ \mathrm{m}^{-1}$		108.687252 ± 0.000158	
$R_e/10^{-10}\ \mathrm{m}$	2.3607701 ± 0.0000076	2.3607755 ± 0.0000076	$2.360796042 \pm 0.000000215$
$\hat{\sigma}$	0.921	0.907	
$F/10^{12}$	7.95	16.3	

[a] Values transformed from function of Ram et al. [7].

In programme Radiatom coefficients $U_{1,0}$, $U_{0,1}$, c_j with $j > 1$ and t_0^{Cl} are directly fitted and other parameters k_e (equilibrium force coefficient), R_e and c_0, with their associated estimated standard errors, are derived indirectly; standard errors associated with k_e and R_e include errors of fundamental constants N_A and h used in their generation [6]. Error propagated to these parameters from uncertainties of atomic masses of Na and Cl, of order $\delta M/M \approx 10^{-7}$ or less, is negligible by comparison with error from other sources. The standard error of R_e estimated with DS-cP is propagated from only spectral data.

5. Discussion

Agreement between values of comparable parameters in Table 2 derived from DS-cP and Radiatom is within combined estimated standard errors of c_0 but deteriorates increasingly for coefficients c_j as j increases; for c_4 the difference of these quantities is about 40 times the individual errors. The reason for these discrepancies is uncertain, but they might reflect to some extent, varied numerical precision; in Radiatom about 30 decimal digits for each real number are carried through the calculations whereas in DS-cP only 15 decimal digits are used. Nevertheless a plot in Fig. 1 of functions $V(R)$ from these two sources shows that they are entirely superimposed on the scale of the figure. A plot of the difference between these two functions, Fig. 2, indicates that this difference is appreciably greater than 50 m^{-1} only near extremes of a range of internuclear distance/10^{-10} m [2.07, 2.77] in which they are defined from available spectral data; these distances mark the classical turning points of the highest purely vibrational state $v = 8$ for which spectral transitions are available. As in the same range of distance the potential energy increases to 280 000 m^{-1} this difference is negligible for all practical purposes. Predictions, from DS-cP and Radiatom, of wavenumbers of hypothetical transitions from the ground vibration–rotational state, with $v'' = 0$ and $J'' = 0$, to highly rotationally excited states with $J' = 115$ and $0 \leq v' \leq 8$ agree within small deviations comparable with the best precisions for observed vibration–rotational transitions involving vibrational states with $v \leq 8$ [7]. Explicitly, the differences between those energies calculated with two independent programmes for the same set of radial parameters differed by less than 0.8 m^{-1} in almost all cases, and by less than 1.5 m^{-1} in the most extreme cases; these differences are comparable with the uncertainties of measured wave numbers of transitions (cf. Table 1). Because of correlations between calculated energies of states, wavenumbers of transitions calculated with the two programmes differed generally by less than these amounts. This test indicates that rotational energies for NaCl generated according to DS-cP conform closely to those calculated according to the standard paradigm.

We tested the effect of extent of expressions $Y_{k,0}$, into which substitutions $\{R_0, a_j\} \rightarrow \{R_J, a_j^J\}$ are made numerically, hence comparing the normalised standard deviation as a function of k. The minimum value of k is 3, as required to include c_4 as a finite value in the fit, which hence corresponds to fourth order. We tested also sixth, eighth and tenth orders (even orders only), hence with $Y_{k,0}$ up to $k = 6$, with c_j being constrained to 0 for $j > 4$. For NaCl the optimum fit is obtained for eighth order, and these results are presented in Table 2. Thus the total number of parameters, either evaluated as presented in Table 2 or set to zero ($c5 = c6 = c7 = c8 = 0$), in DS-cP is eleven.

For comparison with our results we include in Table 2 values of parameters derived by transforming a function of exponential form generated by Ram et al. [7], into the form $V(z)$ in Eq. (7). Both a value of c_0 thus derived and $U_{1,0}$ generated from c_0 are strongly influenced by the value of the equilibrium binding energy D_e that Ram et al. [7], imposed on their function; otherwise values of c_1–c_4 are nearer the corresponding values from Radiatom than from DS-cP, except that c_4 is about midway between our values. For comparison we include in Fig. 1 the original, not trans-

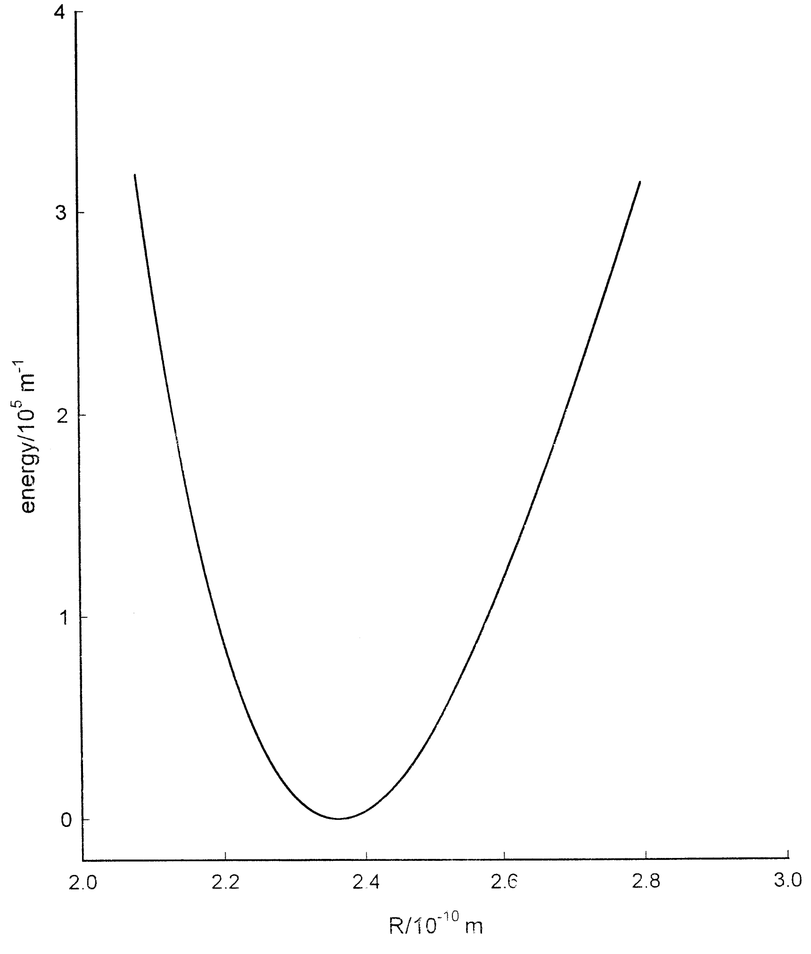

Fig. 1. Plot of potential-energy curves $V(R)$ of NaCl $X^1\Sigma^+$ in the range defined by available spectral data. Three superimposed potential-energy functions are indistinguishable on the scale of this figure.

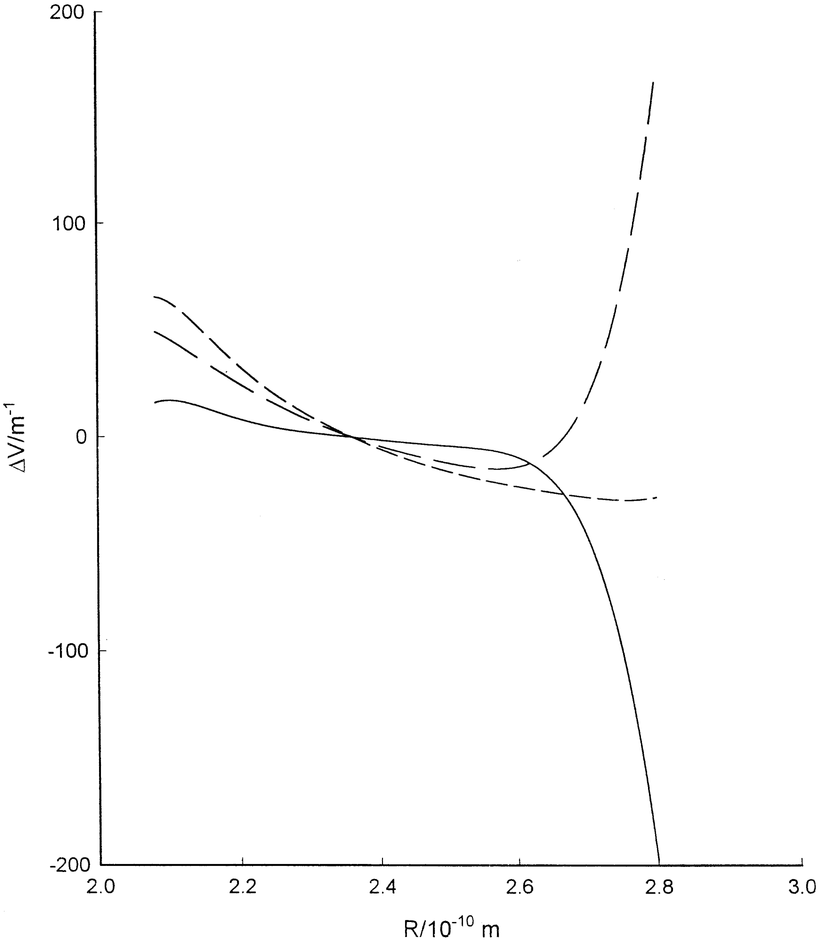

Fig. 2. Plots of difference of potential-energy functions $\Delta V(R)$ in the range defined by available spectral data; the solid line represents $\Delta V(R)$ between results from DS-cP and Radiatom, short dashes, $\Delta V(R)$ between the function of Ram et al. and results from DS-cP, and long dashes $\Delta V(R)$ between the function of Ram et al. and results from Radiatom.

formed, curve $V(R)$ of Ram et al. [7], which is again indistinguishable from our curves within the thickness of the line, and in Fig. 2 the differences between the original $V(R)$ of Ram et al. [7], and our $V(R)$ derived from DS-cP and Radiatom.

The value of R_e derived by Ram et al. [7], has an associated uncertainty much smaller than our estimated standard errors of this parameter, but this condition reflects mostly the presence of t_0^{Cl} among fitted parameters in our set; the latter parameter is poorly evaluated in that $\delta t_0^{\mathrm{Cl}}/t_0^{\mathrm{Cl}} \approx 0.25$, and for this reason also the values of R_e and t_0^{Cl} are highly correlated. Without t_0^{Cl} the value of R_e becomes $(2.36079570 \pm 0.00000020) \times 10^{-10}$ m, and the fitted parameters number six, in agreement with results deduced by Ram et al. [7]; here the unrealistically small uncertainty represents only error propagated from measurements of spectral wave numbers, exclusive of error in h and N_A. A reason for poor evaluation of t_0^{Cl} is simply the finite precision of available spectral data. Like $\Delta_{kl}^{\mathrm{Cl}}$ in Eq. (6), t_0^{Cl} is coefficient of a ratio of electronic and nuclear (or atomic, in practice) masses; for Cl this ratio is 1/70000 or 1.4×10^{-5}. If we seek to have a relative precision $\delta t_0^{\mathrm{Cl}}/t_0^{\mathrm{Cl}} < 0.1$, the concomitant precision of spectral data [15], is required to be $< 1.4 \times 10^{-6}$, which is not generally the case according to Table 1.

We retained t_0^{Cl} among our fitted parameters because lack of a rotational g-factor in sets of parameters employed in analyses of wave numbers of spectral transitions leads to distorted results for R_e. Because we include the effect of g_J through the parameter t_0^{Cl}, even if this is only roughly evaluated, our value of R_e is likely to become more accurate than otherwise, despite the nominally decreased precision. Because spectral data of any isotopic variant of Na are lacking we can not attempt to evaluate t_0^{Na} in the same manner. Parameter t_0^{Cl} the only one indicative of extra-mechanical effects, in particular of nonadiabatic rotational effects. Without t_0^{Cl} our primarily evaluated parameters number six, the same number as those of Ram et al. [7]. Despite a relatively large error of t_0^{Cl}, we employ it to make predictions of rotational g-factors and electric dipolar moment, according to published relations [3]. Fortuitously an estimate of t_0^{Na} from an estimated rotational g-factor and the known electric dipolar moment [23], indicates that its magnitude is nearly 0, whereas typical magnitudes of t_0 have order unity [24]. If accordingly we approximate t_0^{Na} by 0, we predict with t_0^{Cl} from DS-cP that for $^{23}\mathrm{Na}^{35}\mathrm{Cl}$:

$$g_J = -0.041 \pm 0.012$$

$$\mu_e = (27.0 \pm 7.7) \times 10^{-30}\,\mathrm{C\ m} \tag{20}$$

whereas from Radiatom:

$$g_J = -0.032 \pm 0.011$$

$$\mu_e = (21.0 \pm 7.3) \times 10^{-30}\,\mathrm{C\ m} \tag{21}$$

A precise experimental value [23]:

$$\mu_e = (29.9254 \pm 0.0010) \times 10^{-30}\,\mathrm{C\ m} \tag{22}$$

exists for comparison with our dipolar moments, but no experimental value of g_J is available. For $^{23}\mathrm{Na}^{19}\mathrm{F}$ there exists a precise value $g_J = -0.005306 \pm 0.000055$ [25], that has the same sign and roughly the same magnitude as our value of g_J predicted for $^{23}\mathrm{Na}^{35}\mathrm{Cl}$. With dissociation energy $D_0 = 4.23$ eV [26], constrained to conform to the relation [27]:

$$D_e = 4c_0\left(1 + \sum_{j=1} 2^j c_j\right) \tag{23}$$

and the known electric dipolar moment Eq. (22) also imposed as constraint:

$$t_0^{\mathrm{Na}} = t_0^{\mathrm{Cl}} + 2\mu_e/(eR_e) \tag{24}$$

values $t_0^{\mathrm{Na}} = 0.057$, $c_5 = 0.082 \pm 0.009$ and $g_J = -0.042 \pm 0.012$ are derived from a separate fit of spectral data in Table 1 with DS-cP; other parameters adopt values similar to those listed in Table 2. Only coefficients $s_0^{a,b}$ pertaining to the radial factor $\beta(R)$ Eq. (10) can be accommodated within DS-cP at present, but for the present data set this term was redundant.

Our programmes DS-cP and Radiatom seem able thus to produce rough values of quantities pertaining to electric and magnetic properties of diatomic molecules that have not been attempted in another approach, that of Ram et al. [7], based on the same spectral data of NaCl.

Ram et al. [7], justify their use of a potential-energy function of the form:

$$V(R) = D_e\{1 - \exp[-\gamma(R)]\}^2/\{1 - \exp[-\gamma(\infty)]\}^2 \tag{25}$$

in which:

$$\gamma(R) = z\sum_i \gamma_i z^i, \qquad \gamma(\infty) = \sum_i \gamma_i,$$

$$z = (R - R_e)/(R + R_e) \tag{26}$$

by asserting that the full advantage of highly resolved spectra is achieved when extracted spectral information is applicable to prediction of spectra well beyond the range of experimental measurements. Because the portion of the potential-energy function plotted in Fig. 1 extends to less than one tenth of energy at the dissociation limit, extrapolation of the function toward that limit is particularly prone to error. In the case of NaCl that is a strongly polar molecule, the potential-energy function must reflect that property. Like any other known diatomic molecule in its electronic ground state, NaCl dissociates to neutral atoms rather than to ions Na^+ and Cl^-. Although at large internuclear distances the potential energy approaches asymptotically a limit corresponding to dissociation into neutral atoms, at distances less than a critical value R_x, $V(R)$

varies as $-R^{-1}$ reflecting coulombic attraction of otherwise weakly interacting ions Na^+ and Cl^-. That point R_x marks an avoided crossing of hypothetical diabetic curves of potential energy for two states of the same symmetry $^1\Sigma^+$; one is a weakly bound electronic state that correlates with neutral atoms at the dissociation limit and the other is a strongly bound state that correlates with atomic ions with a dissociation limit at a greater energy. As R decreases from R_x towards R_e, the potential energy has almost purely coulombic character [1], but with decreasing internuclear distance between the putative ions, such that their clouds of electronic density begin to overlap significantly, the coulombic contribution to the total potential energy becomes less important; then the shape of the potential-energy curve becomes typical of more covalently bound diatomic molecules in the vicinity of distance R_e, as plotted in Fig. 1. For this reason a function of essentially exponential shape like that of Ram et al. [7], is unlikely to constitute a useful approximation to the true potential energy within the range of internuclear distance/10^{-10} m [4,15], or roughly $1.5R_e < R < 7R_e$; hence predictions of spectral transitions involving vibration–rotational states within a corresponding range of energy according to the potential-energy function of Ram et al. [7], are likely to be grossly unreliable.

In any case with the function of Ram et al. [7], in Eq. (25) the eigenvalues between which spectral transitions occur must be obtained by individual numerical solution of Schrodinger's equation for each vibration–rotational state of each isotopic variant. In contrast all vibration–rotational energies are generated readily from numerical values of term coefficients Y_{kl} and Z_{kl} on merely inserting values of parameters $U_{1,0}, U_{0,1}$, c_j, t_0^{Cl} from Table 2 in the column Radiatom and the pertinent atomic masses into well established expressions of simple form [6]. Moreover, use of such expressions in actual assignments of new spectra has demonstrated conclusively that moderate extrapolation of vibration–rotational energies beyond the range of experimental measurements at a particular stage in an iterative process is entirely practicable [24,28]. For this purpose the set of parameters in column DS-cP of Table 2 are less useful because those values inserted into the standard expressions, equivalent to those of Dunham, produce root-mean-square deviations from experimental wave numbers of transitions of NaCl, 4.4 times the deviations resulting from use of parameters from Radiatom.

The deformationally self-consistent procedure has been justified [5], on the ground that displacements of nuclei in a vibrating and rotating diatomic molecule take place in the vicinity of R_J rather than R_e. Eq. (1) shows that the effective potential energy introduced into the Hamiltonian Eq. (4) solved with quasi-classical or perturbation theory also fulfils exactly this condition. In that sense the procedure called deformationally self-consistent is an alternative approach to fit spectral data. It is remarkable that application of hypervirial perturbation theory [9], in the documented manner yields analytic expressions absolutely identical to those generated with the quasi-classical approach of Dunham [8], and in an extended approach more conducive to symbolic computation [10,11]. In the latter work [29], analytic expressions were generated to evaluate R_J as a function of J in terms of Dunham's parameters for potential energy, according to Eq. (1). In practice not only the approaches embodied in DS-cP and Radiatom but also the purely numerical approach of Ram et al. [7], seem to serve the purpose of reproducing satisfactorily the experimental wave numbers of vibration–rotational transitions. Whichever approach one applies in a given case might then reflect merely personal preference. Among practical aspects of present implementations of our approaches in DS-cP and Radiatom, initial values of parameters fitted according to DS-cP are typically taken from output of Radiatom. In contrast rough values (0 in most cases) generally suffice as initial estimates of parameters for Radiatom, but in some cases convergence of Radiatom according to a stringent internal criterion seems to require excess parameters, which are consequently poorly evaluated. Although a potential-energy function is not an experimentally observable quantity but only a theoretical construct [1], originating in classical mechanics but customarily introduced into some quantum-mechanical formulations, the capability of one or other approach to predict molecular properties or transitions beyond input data for spectral fits, or its ease of use for such applications, might define its practical value in particular conditions.

6. Conclusion

We apply a deformationally self-consistent approach in a programme DS-cP and hypervirial perturbation theory embodied in Radiatom to fit data of wave numbers of vibration–rotational transitions of NaCl so as to yield not only fitting parameters in radial functions but also approximate information about electric and magnetic properties of NaCl molecules, namely the electric dipolar moment and the rotational *g*-factor. This dipolar moment is similar to the known experimental value but there exists no experimental rotational *g*-factor for comparison. Comparison of results from DS-cP and Radiatom for NaCl indicates that Radiatom yields with seven adjusted parameters a negligibly superior fit of these experimental data to DS-cP with eleven parameters (seven adjusted and four constrained to 0).

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