Analysis of Pure Rotational and Vibration-rotational Spectra of NaCl X $^1\Sigma^+$ and Quantum-chemical Calculation of Related Molecular Properties

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We fitted published frequency and wave number data for pure rotational and vibration-rotational spectra, respectively, of ^{23}Na^{35}Cl and ^{23}Na^{37}Cl to derive parameters related to potential energy and to the rotational *g* factor. For comparison with these experimental data we undertook quantum-chemical computation of adiabatic corrections, rotational and vibrational *g* factors, electric dipolar moment and its derivative as a function of internuclear distance in a range near R_e as a test of an algebraic approach to spectral analysis; experimental, 0.0287 ± 0.0014, and calculated, 0.02149, values of g_r at R_e are in moderate agreement. The combined results are discussed from a point of view of computational spectrometry.

Keywords: Spectral analysis; Vibration-rotational spectra; Quantum-chemical calculations; Computational spectrometry; Rotational and vibrational *g* factors.

INTRODUCTION

Sodium chloride has played an important role in the development of infrared spectroscopy since the earliest measurements in the mid infrared region. For instance, Ångstrom used a prism of mineral rocksalt to disperse infrared radiation in his pioneer experiments,[1] and practitioners of infrared spectrometry since that time customarily employ optical components of pure crystalline NaCl such as windows in cells to contain gaseous and liquid samples for spectral examination. The reason is that this compound is inexpensive and transmits light satisfactorily for wave lengths from the ultraviolet region to 16 μm in the mid infrared region. In the farther infrared there is strong absorption of crystalline NaCl with a maximum about 32000 m^{-1} attributed to a lattice vibration, called a transverse optical mode, in which sublattices of atomic centres of types Na and Cl oscillate with opposite phase. Whether these atomic centres correspond essentially to atomic ions or to almost neutral atoms is controversial,[2] but in the gaseous phase at temperatures above 1100 K highly polar diatomic molecules with stoichiometric formula NaCl are a major constituent of vapour over a sample of molten NaCl. Such a heated sample can emit radiation resulting from discrete vibration-rotational transitions from many states thermally populated under those conditions,[3] but spectra in absorption in microwave, millimetre-wave and infrared regions are also readily observable with appropriate instruments.[4-7] For rotational transitions, quantum number *J* for rotational angular momentum alters by only one unit, whereas for all observed vibration-rotational transitions vibrational quantum number *v* concurrently alters by only one unit.[3,6] Reported spectra involve vibrational and rotational states with maximum values $v = 8$ and $J = 118$, respectively.

In an analysis[8] of then available spectra of molecular NaCl for comparison of its parameters with those of other chlorides of elements in group 1 – HCl, LiCl, KCl and RbCl – we assumed a value for the rotational *g* factor, g_r, of ^{23}Na^{35}Cl based on reasonable assumptions according to an analysis of this property known for other molecules in electronic state $^1\Sigma^+$ or 0^+.[9] To ensure that there be no systematic deviation between measured wave numbers of transitions of ^{23}Na^{35}Cl and ^{23}Na^{37}Cl and those calculated on the basis of parameters for potential energy,[10] such information is helpful or even essential. Before the present work, no value of g_r was known for NaCl from either experiment or reliable calculation of molecular electronic structure. The rotational *g* factor is a multipli-

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Dedicated to Professor Ching-Erh Lin on the Occasion of his 66th Birthday and his Retirement from National Taiwan University cand within a factor of proportionality between rotational angular momentum and a net magnetic dipolar moment induced as a result of molecular rotation,[9] but a non-rotating molecule in electronic state $^1\Sigma^+$ or 0^+ possesses no permanent magnetic dipolar moment apart from effects of magnetic nuclei. In contrast a molecule in such an electronic state can possess a net electric dipolar moment, relative to axes fixed in the frame of the molecule; in general for a heteronuclear diatomic molecule there is such an electric dipolar moment, which for NaCl at its equilibrium internuclear separation for the electronic ground state has a value[11] about four fifths that expected for nonpolarizable, or not interacting, Na^+ and Cl^- ions at the same distance. Such a large magnitude of electric moment greatly facilitates observation of pure rotational transitions, because the intensity of the corresponding spectral lines in absorption depends on the square of this quantity. In this way measurements of such transitions have been made for values of rotational quantum number J up to 76 for molecules within vibrational states up to $v = 4$, and with great relative precision.[7] Adding those data to our previous data set for NaCl[8] enables not only an improved and extended evaluation of parameters for potential energy but also an estimate of the rotational g factor. This analysis and related calculations of molecular electronic structure are the subject of this article.

To aid such an analysis and the interpretation of results therefrom, we apply computational spectrometry.[12] By this term we mean the application of results from calculations of molecular electronic structure that can yield information not only about dominant properties pertinent to vibration-rotational spectra, such as total energy and electric dipolar moment that are the principal factors affecting the wave number and intensity of those spectral lines in absorption and emission, but also and more importantly the further molecular properties such as rotational and vibrational g factors that also affect slightly but significantly the wave numbers of transitions; all these properties are readily calculated as a function of internuclear separation R. Although the rotational g factor is a measurable quantity, most directly as a result of splitting, due to the Zeeman effect,[9] of spectral lines for pure rotational transitions, there exists no known magnetic effect of low order that yields comparable information about the vibrational g factor, g_v, but in principle this is an experimentally measurable quantity. Confounding the influence of the latter two quantities are two further terms in an effective hamiltonian $\mathcal{H}(R)$ for motion of atomic nuclei and their associated electrons in a diatomic molecule expressible in this form:[10]

$$\begin{aligned}&\hat{p}\,(1 + g_v(R)\,m_e/m_p)\,\hat{p}\,/(2\mu)\\&\quad + (1 + g_r(R)\,m_e/m_p)\,\hbar^2\,J\,(J+1)/(2\,\mu R^2)\\&\quad + V(R) + V'(R) + V''(R)\end{aligned} \qquad (1)$$

Here $\hat{p}$ is a linear momentum conjugate to a vector to represent instantaneous internuclear separation R, and the next term involves the square of an angular momentum that takes discrete values $\hbar[J(J+1)]^{1/2}$, with J in general a non-negative integer or half integer; $V(R)$ represents the internuclear potential energy that is independent of nuclear mass, m_e is the electronic rest mass and m_p is the protonic mass; $\hbar \equiv h/2\pi$, with Planck's constant h. The vibrational and rotational g factors, with typical magnitudes of both $|g_r|$ and $|g_v| \leq 1$, appear in terms as radial functions $g_r(R)$ and $g_v(R)$ that serve as corrections to the kinetic energy of nuclear motion parallel and perpendicular to the internuclear axis, hence pertaining to vibrational and rotational motions, respectively. Of two further addends in this hamiltonian that have no direct physical significance $V'(R)$ constitutes a radial function for adiabatic corrections to take into account a small dependence on nuclear mass that would otherwise affect $V(R)$, whereas $V''(R)$ constitutes a radial function for nonadiabatic effects further to those within $g_r(R)$ and $g_v(R)$; as $V''(R)$ is expected to be negligible for NaCl we omit it from further consideration. Calculation of $V'(\mathrm{R})$, $g_r(R)$ and $g_v(R)$ is readily practicable through algorithms that have been implemented in suites of computer procedures. As information about only two, at most, of these three radial functions might be gleaned from spectral analysis of data of frequency type in the absence of experiments involving external electric or magnetic field, the function of computational spectrometry is to provide information about one or more of these radial functions so as to enable a physical meaning to be attached to spectral parameters associated with the remaining functions. Because all three contributions to wave numbers of spectral lines have much smaller – but still significant – magnitudes than that from potential energy, the calculation of $V'(\mathrm{R})$, $g_r(R)$ and $g_v(R)$ requires much less accuracy than would the calculation of $V(R)$ to yield an accuracy comparable with that of a measurement of wave number of an actual transition.

ANALYSIS OF SPECTRA

We include in our analysis all reported spectra for pure rotational and vibration-rotational transitions. Early measurements[4] of microwave spectra yielded a few frequencies of lines for pure rotational spectra, four lines for ^{23}Na^{35}Cl up to $v = 3$ and three lines for ^{23}Na^{37}Cl up to $v = 2$, all for $J = 2 \leftarrow J = 1$ and with maximum relative precision $\sim 3 \times 10^{-6}$. Subsequent extension[5] of measurements in a range [7, 24] of J was achieved for 13 lines of ^{23}Na^{35}Cl up to $v = 2$ and six lines of ^{23}Na^{37}Cl up to $v = 1$ but with relative precision $\sim 3\times 10^{-7}$. For vibration-rotational transitions comprising 1184 in total number measured in emission,[3] the maximum value of J is 118 and the maximum value of v is 8; although the maximum relative precision of these measurements for ^{23}Na^{35}Cl is $\sim 6 \times 10^{-6}$, for ^{23}Na^{37}Cl the relative precision was $\sim 10^{-5}$. To the latter data we added 13 unduplicated transitions for ^{23}Na^{37}Cl measured in absorption,[6] with maximum relative precision 2×10^{-6}. A set of these data comprising 1225 unduplicated transitions in total was the subject of our previous analysis.[8] A great extension of pure rotational transitions into the submillimetre range was achieved[7] in measurement of 133 lines of ^{23}Na^{35}Cl and 58 lines of ^{23}Na^{37}Cl, up to $J = 76$ and up to $v = 4$ and maximum relative precision $\sim 3 \times 10^{-8}$. Although the latter range[7] was much greater than for preceding measurements of pure rotational transitions,[4,5] the range of both v and J sampled in vibration-rotational transitions was much greater in turn, as specified above. The principal benefit of the latter pure rotational transitions was their superior precision, which enables a greatly increased sensitivity to isotopic effects associated with atomic centre Cl.

As a basis of analysis of these data we applied this formula[10] for discrete values of energy E_{vJ}^{i} for a particular isotopic species, consistent with the effective hamiltonian above:

$$h\,c \sum_{k=0}^{\infty}\sum_{l=0}^{\infty} \left(Y_{kl} + Z_{kl}^{v,Na} + Z_{kl}^{v,Cl} + Z_{kl}^{r,Na} + Z_{kl}^{r,Cl}\right) (v + 1/2)^{k}\,[J\,(J + 1)]^{l} \qquad (2)$$

Apart from velocity of light c, in this formula Dunham coefficients Y_{kl} take into account the major effects corresponding to mechanical motions of vibration and rotation of two atomic nuclei and their associated electrons about the centre of molecular mass, and auxiliary coefficients Z_{kl}, of two types, take into account the extra-mechanical effects whereby electrons fail to follow perfectly one or other atomic nucleus in its vibrational and rotational motion. Extra-mechanical effects[10] are separable into vibration-rotational contributions, in Z_{kl}^{v}, and further rotational contributions, in Z_{kl}^{r}; coefficients of both these types have a dependence on inverse mass of separate atomic centres, thus either Na or Cl, whereas coefficients Y_{kl} depend on the reduced mass of the molecule as a whole.

The relation[10] between these term coefficients of types Y_{kl} and Z_{kl} and terms in an effective hamiltonian arises from the expression of the latter terms as radial functions, thus of internuclear separation R or a selected functional of R; in the present case we employ a reduced displacement variable z defined as

$$z = 2\,(R - R_e)/(R + R_e) \qquad (3)$$

We define four radial functions in terms of this variable, for potential energy,

$$\mathrm{V}(z) = V_0 + h\,c\,c_0\,z^2\,(1 + \sum_{j=1} c_j\,z^j) \qquad (4)$$

for the vibrational g factor,

$$g_v(z) = m_p\,(\sum_{j=0} s_j^{Na}\,z^j / M_{Na} + \sum_{j=0} s_j^{Cl}\,z^j / M_{Cl}) \qquad (5)$$

for the rotational g factor,

$$g_r(z) = m_p\,(\sum_{j=0} t_j^{Na}\,z^j/M_{Na} + \sum_{j=0} t_j^{Cl}\,z^j/M_{Cl}) \qquad (6)$$

and for adiabatic corrections.

$$\mathrm{V}'(z) = h\,c\,m_e\,(\sum_{j=0} u_j^{Na}\,z^j/M_{Na} + \sum_{j=0} u_j^{Cl}\,z^j / M_{Cl}) \qquad (7)$$

For NaCl in its electronic ground state X $^1\Sigma^+$ that is our present concern, $V_0 \equiv 0$; both g_v and g_r are calculated as sums of electronic and nuclear contributions: the nuclear contribution depends on only atomic numbers and atomic masses, whereas the electronic contribution is calculated formally as a sum of squares of matrix elements of nuclear operators over electronically excited states, called nonadiabatic effects. Adiabatic corrections are calculated as the corresponding expectation values within the electronic ground state. No part of the expression for potential energy depends on nuclear mass, but expressions for vibrational and rotational g factors and for adiabatic corrections depend on masses of separate atomic centres as indicated, and include also a ratio of electronic and atomic masses; for the adiabatic corrections we ignore the difference between a nuclear and an atomic mass of a given nuclide. Coefficients $t_j^{Na,Cl}$ can be related to coefficients p_j in a radial function for electric dipolar moment of this form:[9]

$$\mathrm{p}(z) = \sum_{j=0} p_j\,z^j \qquad (8)$$

Involving the value of the rotational g factor at R_e and the corresponding value of $p(R_e)$ for which $z = 0$, the relations pertinent to analysis of data of NaCl are

$$t_0^{\mathrm{Na}} = \mu\,[g_r(R_e)/m_p - 2\,p_0/(e\,R_e\,M_{\mathrm{Cl}})] \tag{9}$$

and

$$t_0^{\mathrm{Cl}} = \mu\,[g_r(R_e)/m_p + 2\,p_0/(e\,R_e\,M_{\mathrm{Na}})] \tag{10}$$

In particular, Dunham coefficients[13] Y_{kl} depend on reduced mass μ,

$$\mu = M_{\mathrm{Na}}\,M_{\mathrm{Cl}}/(M_{\mathrm{Na}} + M_{\mathrm{Cl}}) \tag{11}$$

equilibrium internuclear separation R_e and coefficients c_j in $V(z)$. Auxiliary coefficients of type $Z_{kl}^{v,\mathrm{Na}}$ depend on the preceding parameters plus M_{Na} and coefficients s_j^{Na} in $g_v(z)$ and u_j^{Na} in $V'(z)$, and analogously for $Z_{kl}^{v,\mathrm{Cl}}$, whereas coefficients of type $Z_{kl}^{r,\mathrm{Na}}$ depend likewise on parameters within Y_{kl} plus M_{Na} and coefficients s_j^{Na} in $g_v(z)$ and t_j^{Na} in $g_r(z)$, and analogously for $Z_{kl}^{r,\mathrm{Cl}}$. All these expressions are reported explicitly elsewhere.[10] An important aspect of an application of Dunham's formalism[13] is that Dunham coefficients Y_{kl} and auxiliary coefficients Z_{kl} of various types, in consistent sets, number minimally to reproduce satisfactorily the wave numbers in the full data set on conducting a simultaneous fit of both pure rotational and vibration-rotational transitions of all isotopic species; further such coefficients Y_{kl} and Z_{kl} are set to zero. The evaluated coefficients imply values of R_e plus radial coefficients of types c_j, s_j, t_j and u_j in finite sets that thereby become evaluated; further radial coefficients are entirely undefined, but are unlikely to have zero values. For application to spectra of NaCl, because available spectra involve only ^{23}Na, there is no possibility of evaluating coefficients s_j^{Na}, t_j^{Na} and u_j^{Na} directly from experimental data of only wave-number type, but either indirect methods or application of results from quantum-chemical calculations is feasible.

In analysis of spectra of NaCl we first fitted all transitions except the pure rotational data[7] with transitions involving large J. Thus for 17 pure rotational and 1206 vibration-rotational transitions of ^{23}Na^{35}Cl and ^{23}Na^{37}Cl within ranges $v \le 8$ and $J \le 120$, six independent fitted parameters, specifically R_e and c_0-c_4, with two constrained parameters – $t_0^{\mathrm{Na,Cl}}$ estimated, according to formulae 9 and 10, from electric dipolar moment[11] and g_r at R_e factor taken to be zero – suffice to reproduce the wave numbers for which the best relative precision[8] is 3×10^{-7}. These parameters appear in the first column of Table 1. The corresponding value of reduced standard deviation $\hat{\sigma}$ of this fit is 0.921; that this value is less than unity indicates that precisions of measurements are estimated conservatively. Although those radial coefficients in Table 1 might be considered to possess a physical meaning in relation to their respective radial functions, one must bear in mind that the purpose of these coefficients is to ensure a consistent

Table 1. Coefficients of radial functions and other molecular parameters of NaCl X $^1\Sigma^+$, depending on extent of data set and constrained parameters

Parameter	1223 data, [t_0^{Na}, t_0^{Cl}]	1412 data, [t_0^{Na}, t_0^{Cl}]	1412 data, [t_0^{Na}]	1428 data, [t_0^{Na}, u_j^{Na}, u_j^{Cl}]
c_0/m^{-1}	15247257 ± 18	15247401 ± 22	15247425 ± 24	15247678 ± 22
c_1	-2.076785 ± 0.000037	-2.0768284 ± 0.0000095	-2.0768239 ± 0.0000095	-2.0767952 ± 0.0000102
c_2	2.54160 ± 0.00027	2.53836 ± 0.00048	2.53836 ± 0.00048	2.537935 ± 0.00048
c_3	-1.8567 ± 0.0020	-1.84459 ± 0.00162	-1.84459 ± 0.00162	-1.84411 ± 0.00169
c_4	-0.2888 ± 0.0176	0.0198 ± 0.042	0.0195 ± 0.042	0.0747 ± 0.044
c_5	...	1.97 ± 0.29	1.975 ± 0.29	1.635 ± 0.29
c_6	...	-2.21 ± 0.41	-2.22 ± 0.41	-2.697 ± 0.47
s_0^{Cl}	...	...	-0.238 ± 0.032	-2.718 ± 0.037
t_0^{Na}	[0.81]	[0.81]	[0.727]	[1.0225]
t_0^{Cl}	[-0.77]	[-0.77]	-0.8527 ± 0.0082	-0.5598 ± 0.0096
t_1^{Cl}	...	-1.685 ± 0.067	...	...
$u_1^{\mathrm{Cl}}/10^6$ m^{-1}	...	-1.240 ± 0.126	...	[a]
$U_{0,1}$/m^{-1} u	302.465982 ± 0.000047	302.466455 ± 0.000039	302.467076 ± 0.000039	302.469618 ± 0.000045
$U_{1,0}$/m^{-1} u^{½}	135820.124 ± 0.091	135820.873 ± 0.106	135821.120 ± 0.115	135822.819 ± 0.110
$R_e/10^{-10}$ m	2.36080425 ± 0.00000058	2.36080240 ± 0.00000057	2.36079998 ± 0.00000057	2.36079006 ± 0.00000058
k_e/N m^{-1}	108.687209 ± 0.000147	108.688406 ± 0.000171	108.688801 ± 0.000184	108.691521 ± 0.000177
$\hat{\sigma}$	0.921	0.880	0.881	1.032

[a] Coefficients u_j^{Na} and u_j^{Cl} are constrained to values presented in Table 3.

and minimal set of Dunham coefficients[13] Y_{kl} and auxiliary coefficients[10] Z_{kl} that they represent, and that alternative means[14,15] to derive these Dunham coefficients involve no such radial functions, which become accordingly artefacts of a particular mathematical model.

Despite the fact that an additional 189 pure rotational lines[7] involve in their assignments quantum numbers, specifically $v \leq 4$ and $J \leq 76$, that are well within the total ranges of v and J of the vibration-rotational transitions,[3,6] their wave numbers are unsatisfactorily reproduced, relative to their precision of measurement that is 3×10^{-8} at best, with only those eight parameters. We accordingly made further fits including those 189 pure rotational lines of both isotopic species;[7] with retention of two constrained parameters $t_0^{\mathrm{Na,Cl}}$, not only c_5 and c_6 for potential energy, reflecting enhanced sensitivity of the entire set of data to effects of centrifugal distortion, but also a parameter t_1^{Cl} related to the rotational g factor and parameter u_1^{Cl} associated with adiabatic corrections, reflecting enhanced sensitivity of additional data to isotopic effects associated with Cl, become thus evaluated. These results appear in the second column of Table 1. The value of $\hat{\sigma}$ for this fit differs immaterially from that of the preceding fit. Comparison of values of parameters between the first two columns of Table 1 indicates that, except c_4, only small alterations occur; hence for corresponding parameters these fits are reasonably stable. There is no indication that further nonadiabatic effects, present within $V''(R)$ in the effective hamiltonian, are required to be taken into account in this fit, consistent with $(m_e/\mu)^2 \sim 10^{-9}$ for NaCl being smaller than the best precision.

Because the additional pure rotational data[7] are so precise, in a further fit we avoided constraining a value of t_0^{Cl}, but discovered a further parameter, of which s_0^{Cl} seemed best, to be also necessary; results appear in the third column of Table 1. With a known precise value[11] of p_0 of ^{23}Na^{35}Cl and our fitted value of t_0^{Cl} inserted in formulae 9 and 10, we estimate $g_r(R_e) = 0.00741 \pm 0.00060$ and t_0^{Na}; the latter value was included as a constraint in iterative fitting until convergence was attained. This value of g_r for ^{23}Na^{35}Cl is a genuine prediction as no value was known from other experiment or calculation at the time of these fits, but its reliability rests on the assumption of negligible adiabatic corrections.

QUANTUM-CHEMICAL CALCULATION OF MOLECULAR PROPERTIES

For this reason, we calculated adiabatic corrections with a wave function of type multi-configuration, self-consistent field (MCSCF)[16] and complete active space (CASSCF)[17] with eight electrons in thirteen orbitals – five σ, three π and one δ orbitals – included in the active space and using (17s12p5d4f|7s6p4d3f) contractions for Na and Cl with the ANO basis sets.[18] The reported values are calculated with numerical differentiation, performed with the Westa program,[19] of MCSCF wave functions and a local development version of Dalton.[20]

We express direct results of adiabatic corrections at each internuclear distance R in the following form:

$$V'(R)/h\,c = \Delta V^{\mathrm{Na}}(R)/M_{\mathrm{Na}} + \Delta V^{\mathrm{Cl}}(R)/M_{\mathrm{Cl}} \qquad (12)$$

Values of $\Delta V^{\mathrm{Na,Cl}}$ and of the total $V'(R)/hc$ of ^{23}Na^{35}Cl for ten selected values of R appear in Table 2. We fitted those values of $\Delta V^{\mathrm{Na,Cl}}$ to a polynomial in z to evaluate coefficients $u_j^{\mathrm{Na,Cl}}$ consistent with formula 7; for a quartic and a cubic polynomial sufficient to reproduce satisfactorily the calculated points, the resulting coefficients appear in Table 3. The internuclear distances selected for these calculations emphasize the range near R_e and all lie within the range of a strongly polar molecule, because the point of an avoided crossing of the curve for the electronic ground state of NaCl with another curve for potential energy in an electronically excited state

Table 2. Adiabatic corrections ΔV for atomic centres Na and Cl and total adiabatic correction $V'(R)$ for NaCl X $^1\Sigma^+$ as a function of internuclear separation R

$R/10^{-10}$ m	$\Delta V^{\mathrm{Na}}/10^2$ u m^{-1}	$\Delta V^{\mathrm{Cl}}/10^2$ u m^{-1}	$V'(R)/h\,c$ m^{-1}
1.0000	17262.3	45717.5	112.911
2.0000	16986.5	45651.1	112.149
2.2200	16976.1	45645.8	112.116
2.2800	16974.3	45644.9	112.110
2.3608	16972.3	45644.0	112.104
2.4400	16970.7	45643.3	112.099
2.5200	16969.3	45642.7	112.095
3.0000	16964.4	45641.6	112.083
4.0000	16962.6	45642.2	112.078
8.0000	16961.9	45643.4	112.078

Table 3. Coefficients u_j for adiabatic corrections for atomic centres Na and Cl in NaCl X $^1\Sigma^+$

j	$u_j^{\mathrm{Na}}/10^6$ m^{-1}	$u_j^{\mathrm{Cl}}/10^6$ m^{-1}
0	3093.8508 ± 0.0062	8320.4066 ± 0.0158
1	-9.908 ± 0.109	-4.468 ± 0.180
2	26.96 ± 0.26	10.260 ± 0.113
3	-36.95 ± 0.21	-5.75 ± 0.23
4	17.54 ± 0.32	0

also of symmetry class $^1\Sigma^+$ is ~11 × 10^{-10} m. The difference in energies between these electronic states for internuclear distances within the range of this domain, for instance near ~8 × 10^{-10} m, is small enough to cause problems in calculations of adiabatic effects that hence require careful handling.

With program package[20] Dalton 1.2 for computation of molecular electronic structure and molecular properties in another developmental version, we calculated also the rotational g_r and vibrational g_v factors, electric dipolar moment p and its derivative dp/dR with respect to internuclear distance with wave functions[16,21] of type multi-configurational, self-consistent field and complete active space[17] (CAS). The calculation of rotational[9,22-33] and vibrational[32,33] g factors using linear-response theory and details of an implementation of the rotational g factor using rotational London orbitals,[34] the vibrational g factor[32] and the derivative of electric dipolar moment[35] is described in general aspects elsewhere. We initiated calculations with a complete active space and natural orbitals obtained on diagonalizing the one-electron density matrix evaluated through second order in Møller-Plesset perturbation theory[36,37] (MP2). The complete active space comprised MP2 natural orbitals $7\sigma^+$-$11\sigma^+$, 3π-5π and 1δ, whereas MP2 natural orbitals $1\sigma^+$-$6\sigma^+$ and 1π-2π were kept doubly occupied throughout these CAS calculations. The basis set employed is based on polarized basis sets of medium size.[38,39] Because these basis sets are known[40] to be insufficiently flexible for accurate calculation of magnetic properties, we suppressed completely the contraction of basis functions and added additional polarization functions, of *d*-type, and second polarization functions, of *f*-type, with exponents in the same set as the *p*-functions according to a philosophy of medium-sized polarized basis sets; the exponents of the additional functions are presented in Table 4, and results for ^{23}Na^{35}Cl at five internuclear distances are presented in Table 5.

At each distance the value of the total vibrational g factor is notably larger than that of the rotational g factor. The nuclear contribution to both g factors is positive and constant, 0.48502, whereas the electronic contributions are both negative. The absolute value of the electronic contribution is hence slightly larger for the rotational g factor than for the vibrational g factor, contrary to what is found for H_2[32] and HeH^+,[33] for which near R_e the electronic contribution to g_v was four to seven times as large as the electronic contribution to g_r. Moreover, relative to the nuclear contribution, the electronic contributions to both g_r and g_v are larger than for H_2 and HeH^+; the total g factors are thus much smaller for NaCl than for those molecular species, which implies that the electrons follow more closely the motion of one or other associated atomic nucleus.

Table 4. Exponents of additional first and second polarization functions

Type	Na	Cl
d	0.0163	6.5995
	0.0057	2.7141
f	0.0465	0.3580
	0.0163	0.1250
	0.0057	0.0436

Table 5. Calculated rotational g factor, g_r, vibrational g factor, g_v, electric dipolar moment, p, and its gradient, dp/dR, for ^{23}Na^{35}Cl in electronic state X $^1\Sigma^+$ as a function of internuclear separation R

$R/10^{-10}$ m	g_r	g_v	$p/10^{-30}$ C m	$dp/dR/10^{-20}$ C
2.2200	0.02003	0.06080	-28.442	-13.105
2.2800	0.02076	0.05974	-29.240	-13.458
2.3608	0.02149	0.05845	-30.345	-13.894
2.4400	0.02200	0.05731	-31.461	-14.282
2.5200	0.02234	0.05628	-32.618	-14.638

DISCUSSION

Potential energy

Parameters c_0-c_6 in Table 1 define a radial function for internuclear potential energy independent of mass; this function is precisely what one expects to result from an exact quantum-mechanical calculation of total molecular electronic energy, including internuclear repulsion, at each fixed internuclear distance in a domain/10^{-10} m [2.09, 2.79]. End points of that domain are approximately the classical turning points of nuclear oscillation for vibrational state $v = 8$ of ^{23}Na^{35}Cl, which is the most energetic vibrational state for which experimental data are included in the present data set. That quantum-mechanical calculation must include ‘relativistic effects’ that are naturally embodied within experimental data, so hence become an artefact of approximate computational approaches. The equilibrium internuclear distance $R_e/10^{-10}$ m = 2.36079998 ± 0.00000057 presented in Table 1 has a relative uncertainty 0.24 parts per million, most of which results from uncertainty in fundamental physical constants h and N_A that are involved in a conversion of spectral parameter $U_{0,1} \equiv Y_{0,1}\mu$ into that distance. That uncertainty in R_e is also about 1 per cent of either nuclear diameter. For comparison the atomic masses[41] of ^{23}Na and ^{35}Cl have relative precisions 1.3×10^{-4} and 1.1×10^{-3} ppm, respectively. For a quantum-mechanical calculation to yield values of differences of vibration-rotational energies comparable with experiment, that calculation must achieve a relative precision $\sim 3 \times 10^{-8}$ on a basis of the best measurements of rotational frequencies or at least $\sim 1.6 \times 10^{-6}$ on a basis of $\delta c_0/c_0$ for which values appear in Table 1.

To facilitate acquiring an understanding of molecular properties and spectral phenomena from a spectral analysis, an advantage of this data set of NaCl is that measurements of spectral wave numbers encompass maximum ranges [0, 8] of vibrational quantum number v and [0, 118] of rotational quantum number J. Although that level $J = 118$ is attained for only one vibrational state, $v = 1$, for other vibrational states up to $v = 6$ the rotational excitation is almost as great. For vibrational states $v = 7$ and 8, the extents of rotational excitation are $J = 82$ and 75, respectively. Each rotational state is formally characterised with its own function of effective potential energy, defined as a sum of rotationless potential energy and a centrifugal term,

$$\mathrm{V}_{\mathrm{eff}}\,(R, J) = \mathrm{V}(R) + h\,c\,B_{\mathrm{e}}\,J\,(J+1)\,R_{\mathrm{e}}^{2}/R^{2} \tag{13}$$

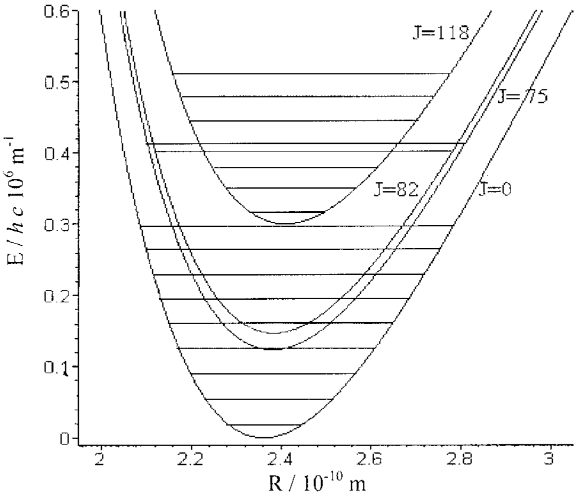

Fig. 1. Curves of effective potential energy $\mathrm{V}(R)/h\,c + B_{\mathrm{e}}\,J\,(J+1)\,R_{\mathrm{e}}^{2}/R^{2}$ for $J = 0$, 75, 82 and 118 in order of increasing energy for ^{23}Na^{35}Cl in electronic ground state X $^1\Sigma^+$; the ordinate axis indicates energy/$h\,c$ 10^6 m^{-1} relative to the minimum of potential energy. The lower manifold of horizontal lines indicates energies of pure vibrational states for $v = 0,1,\ldots 8$; the upper manifold of horizontal lines applies to approximately the rotational state of experimentally sampled greatest energy within a particular vibrational state: thus a curve for $J = 118$ supports vibrational states v = 0-6, whereas a curve for $J = 82$ supports $v = 7$ and a curve for $J = 75$ supports $v = 8$. On the scale of the figure the energy of state $v = 3$, $J = 118$ coincides with that of state $v = 8$, $J = 75$.

In Fig. 1 we present a graph that exhibits curves of effective potential $\mathrm{V}_{\mathrm{eff}}\,(R, J)/h\,c$ for $J = 0$, 75, 82 and 118. Horizontal straight lines within these curves denote energies of pure vibrational states in the lower manifold pertaining to $J = 0$ and of approximately maximum observed vibration-rotational states for $J = 75$, 82 and 118; the energy of state $v = 3$, $J = 118$ practically coincides with that of state $v = 8$, $J = 75$. Inclusion of that centrifugal term within the effective potential might produce a maximum in the curve for $R > R_{\mathrm{e}}$, but all such curves possess the same asymptotic limit for large R; for $J = 118$ this maximum energy occurs at $\sim 7.2 \times 10^{-10}$ m, at which point, not shown in Fig. 1, the difference between curves for $J = 118$ and $J = 0$ is $\sim 3 \times 10^4$ m^{-1}.

Another result of this analysis of vibration-rotational spectra of NaCl is the production of a precise value of the equilibrium force coefficient, $k_{\mathrm{e}}/\mathrm{N\,m^{-1}} = 108.688801 \pm 0.000184$, which is about one fifth that of HCl, both for electronic ground states of symmetry class $^1\Sigma^+$; the equilibrium binding energies $\mathrm{D_e}/10^6\,h\,c\,\mathrm{m}^{-1}$ of NaCl and HCl are 3.43 and 3.575, respectively. Despite the similarity in binding energies, these force coefficients exhibit a disparity that might be associated with varied characters of binding, largely ionic for NaCl but largely covalent for HCl. Even at $v = 8$ the vibrational energy of NaCl within electronic state X is only 0.087 $\mathrm{D_e}$, and remains less than the energy of the most energetic rotational state observed for $v = 0$, as demonstrated in Fig. 1.

Inclusion of adiabatic corrections in fits of spectral data

Our prediction that $g_{\mathrm{r}}(R_{\mathrm{e}}) = 0.00741 \pm 0.00060$ is predicated on a supposition that adiabatic corrections have small magnitudes relative to the effect of the rotational g factor. With calculated values of adiabatic corrections in Table 2 we can test that supposition. In precise terms, we must compare contributions to $Z_{0,1}$ for both atomic centres Na and Cl from adiabatic effects and from g_{r}. With values of parameters in the third column of Table 1 and known expressions for these auxiliary term coefficients, for ^{23}Na^{35}Cl we find these contributions/m^{-1} to be -0.00034 and 0.00038 for Na and 0.000046 and -0.00029 for Cl. Although the former magnitudes for Na are similar, they are irrelevant because lack of data for an isotopic species other than ^{23}Na precludes fitting t_0^{Na} in any case. The magnitude of the contribution of the adiabatic correction to $Z_{0,1}$ is only one sixth that from g_r, but that extent might be significant. For this reason we made further fits of 1428 spectral data, including all data from absorption measurements[6] and eliminating duplicated data from emission spectra,[3] and included all u_j^{Na} and u_j^{Cl} from Table 3 as fixed parameters; with t_0^{Na} at a value constrained to reproduce the electric dipolar moment of $^{23}Na^{35}Cl$ at R_e,[11] the results of a fit appear in the fourth column of Table 1. On the basis of the fitted value of t_0^{Cl}, we thus produce an estimate $g_r(R_e) = 0.0287 \pm 0.0014$ with hence a larger magnitude than before. In the case of either 0.00741 or 0.0287, the magnitude is smaller than typical magnitudes for alkali halides, but is comparable with that of $^{23}Na^{19}F$ for which $g_r = -0.00536 \pm 0.00006$ [9] with an opposite sign. The value of $\hat{\sigma}$ for the latter fit is larger than for the preceding columns of Table 1 because estimates of uncertainties of measurements of wave number are more realistic for the absorption spectra[6] than for the emission spectra.[3]

The latter estimate $g_r(R_e) = 0.0287 \pm 0.0014$, which amounts still to a prediction because it was derived separately from the results of quantum-chemical calculations, is about a third, or five estimated standard errors, larger than the accurate computational value in Table 5, $g_r(R_e) = 0.02149$, although the order of magnitude and sign are correct. We attribute this discrepancy to accumulated error in spectral data and truncation of series. Although the values of ΔV^{Cl} in Table 2 are likely accurate to about one part in 1000, those values for internuclear distance near R_e vary only slightly with R; nevertheless the slope, $u_1^{Cl}/10^6\ m^{-1} = -4.468 \pm 0.180$, of the radial function in the contribution to $V'(z)$, which is a critical parameter for the fitting of t_0^{Cl}, appears satisfactorily defined. From values of coefficients p_j in formula 8 derived from results in Table 5 and g_v therein, we expect $s_0^{Na} = 0.688$ and $s_0^{Cl} = -1.047$; as there are no data for an isotopic variant of Na other than ^{23}Na, the value of s_0^{Na} is inaccessible from our spectral analysis, but the derived value of s_0^{Cl} present in the fourth column of Table 1 differs markedly from that expected value. As for H_2,[32] estimation of the rotational g factor appears easier than for the vibrational g factor.

CONCLUSION

Our practice here of computational spectrometry, whereby results from calculation of adiabatic corrections are applied as constraints to obtain reliable values of rotational and vibrational g factors through their respective radial coefficients s_j and t_j in formulae 6 and 5, respectively, has produced an experimental value of $g_r(R_e)$ near that of our calculations, confirming the validity of our algebraic approach to spectral analysis. Our calculations of rotational and vibrational g factors and adiabatic corrections as a function of internuclear distance near the equilibrium separation provide a significant addition to our knowledge of these properties of diatomic molecules, within a context of an effective hamiltonian in formula 1.

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