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Precise Potential-energy Function for the $X^{-1}\Sigma^{+}$ State of Hydrogen Chloride

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Data for frequencies and wavenumbers of 896 rotational and vibrational-rotational transitions of gaseous hydrogen chloride, ${}^{1}H^{35}Cl$, ${}^{1}H^{37}Cl$, ${}^{2}H^{37}Cl$, ${}^{2}H^{37}Cl$, in the ground electronic state $X^{1}\Sigma^{+}$ have been analysed according to a method of stepwise merging in order to generate a precise potential-energy function essentially free of mass dependence, up to 0.52 of the dissociation limit. This dependence of the Born–Oppenheimer potential energy upon internuclear separation is given both in numerical form (R.K.R. method) and analytically according to the Dunham series expansion. Seven mass coefficients and 24 energy coefficients in mass-reduced form suffice to reproduce satisfactorily not only the fitted 896 frequencies and wavenumbers but also other data of ${}^{3}HCl$ and ${}^{1}H^{37}Cl$ not included in the fitting procedure.

Since the pioneering investigations in infrared spectroscopy, the vibrationalrotational band spectra of gaseous hydrogen chloride, together with its isotopic molecules, have been a frequent topic of investigation. Burmeister¹ distinguished two maxima in the absorption spectrum of HCl at 3.40 and $3.55 \,\mu m$, now known to pertain to the R- and P-branch envelopes, respectively, in the fundamental band, $v = 1 \leftarrow v = 0$. Within a year von Bahr² discovered twelve absorption maxima belonging to different rotational transitions in the same band; using the quantummechanical version of the theory of Bjerrum and Rutherford for the nuclear atom, von Bahr was able to calculate a rotational frequency and a moment of inertia that would have led to a bond length of 1.25×10^{-10} m. Randall and Imes³ discovered a set of satellite lines in the first overtone band, $2 \leftarrow 0$, that were attributed to ¹H³⁷Cl, accompanying the more intense lines of ¹H³⁵Cl. Later work by Rank *et al.*, ⁴⁻⁶ Webb and Rao^{7,8} and Levy *et al.*⁹ on the absorption spectra of the heated gases provided data that not only made observable more rotational structure but also made possible measurement of lines originating in the $v \leq 3$ states of ¹HCl and the first measurements for ²HCl. With the advent of high-resolution interferometers operating in the infrared region, exploitation of these instruments to obtain new measurements of vibrational-rotational spectra of the hydrogen halides was possible. In the case of ¹HCl and ²HCl, not only have improved spectral parameters been obtained for the free molecules, ¹⁰⁻¹² but also a precise examination of pressure-induced shifts has been permitted.¹³ Other recent direct absorption measurements of other overtones, up to $7 \leftarrow 0$, have been made in the visible region either by use of long-path cells¹⁴ or by laser techniques^{15,16} with intracavity samples.

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In addition to these extensive data from vibrational-rotational spectra in absorption, complementary information is available from both emission and pure rotational spectra. Emission spectra have been obtained from HCl gas stimulated in an electric discharge¹⁷ and from the chemiluminescent reaction of atomic hydrogen with molecular chlorine, first under moderate resolution¹⁸ and later with greatly improved dispersion.¹⁹ Pure rotational transitions have been measured by both frequency methods^{20,21} in the millimetre-wave region and by wavenumber methods^{22,23} for laser-active transitions in the far infrared.

From the preceding review, it is clear that an extensive collection of spectrometric data is now available for the several known isotopic molecules of HCl in the electronic ground state. Each contribution in the collection is characterised by a particular precision of measurement and by different sources and extents of experimental inaccuracy. Our objective in the present work has been to perform a statistically rigorous inversion of the more reliable of the data to a set of isotopically invariant parameters (U_{kl}, Δ_{kl}) that reproduce closely the measured data of wavenumbers and frequencies of all the isotopic molecules, and hence also lead to the single isotopically invariant potential-energy function corresponding to the Born-Oppenheimer approximation. This dependence of potential energy on internuclear separation, R, has been expressed both numerically, according to the R.K.R. method,^{24^{*}} and analytically, according to the Dunham function²⁵ in terms of a truncated set of coefficients a_i of the reduced internuclear separation $x \equiv$ $(R - R_{\rm e})/R_{\rm e}$:

$$V(x) = a_0 x^2 \left(1 + \sum_{i=1}^8 a_i x^i \right).$$
 (1)

A reliable description of the potential-energy function is an essential foundation on which analysis of other spectrometric data, such as intensities, can be made.

In terms of the reduction of the experimental wavenumbers to mass-reduced parameters, our approach is similar to that of Guelachvili et al.¹² Both treatments employ the theoretical isotopic dependence²⁶ of the Dunham energy coefficients Y_{kl} that are used to represent the term values E(v, J) of particular isotopic molecules:

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

Our treatment has, however, included transitions in a considerably larger range of energy, up to states with v = 7, compared with $v \le 3$ in the earlier work.¹² Furthermore our approach to the weighted fitting of the data is based on the principles of stepwise merging.²⁷ An important consequence of this different approach is that the present estimates of parameters reproduce the entire data much better than those of Guelachvili *et al.*¹²

The earlier values²⁸ of potential-energy coefficients a_i were derived from the relatively imprecise parameters Y_{kl} of ¹H³⁵Cl determined by Rank *et al.*⁶ The availability of more extensive expressions²⁹ relating the energy coefficients, U_{kl} or Y_{kb} to the potential-energy coefficients a_i has facilitated our reduction to an improved set of a_i . A novel feature of our iterative inversion of the U_{kl} set has been the incorporation of information from the R.K.R. calculation.

THEORETICAL BACKGROUND

The vibrational-rotational term values for a particular isotopic dinuclear molecule i in a ${}^{1}\Sigma$ electronic state can usually be represented adequately by the

power series in vibrational (v) and rotational (J) quantum numbers

$$E^{i}(v,J) = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} Y^{i}_{kl} (v + \frac{1}{2})^{k} [J(J+1)]^{l}.$$
 (3)

Exceptions occur for perturbed states or weakly bound molecules, and for states near a dissociation limit. If data are available for several isotopically related molecules, the Y_{kl}^{i} quantities are related approximately by

$$Y_{kl}^{i} = \mu_{i}^{-(k+2l)/2} U_{kl} \tag{4}$$

in which μ_i is the reduced mass of the *atoms* of the isotopic molecule *i* and the U_{kl} quantities are isotopically invariant. The failure of eqn (4) to describe accurately the isotopic variation of precisely determined Y_{kl}^i values has been the subject of several theoretical treatments. Watson recently showed²⁶ that for a neutral molecule

$$Y_{kl}^{i} = \mu_{i}^{-(k+2l)/2} U_{kl} [1 + m_{e} (\Delta_{kl}^{a} / M_{a} + \Delta_{kl}^{b} / M_{b})],$$
(5)

in which m_e is the mass of the electron, and M_a and M_b are the masses of the separated neutral atoms a and b. This expression is a much better, and in practice quite adequate, representation of the isotopic dependence of $Y_{kl}^i \mu_i^{(k+2l)/2}$. Bunker³⁰ had obtained a similar expression for only the cases of Y_{01} and Y_{10} . Eqn (5) takes account of the two effects of comparable magnitude (both of order m_e/M) which cause eqn (4) to be inadequate, namely failure of the Born–Oppenheimer separation of electronic states and the quantum effects originally discussed²⁵ by Dunham, commonly termed Dunham corrections. In eqn (5), $\Delta_{kl}^{a,b}$ are isotopically invariant parameters without straightforward physical interpretation; their magnitude is, however, expected to be of order unity.²⁶ Defining

$$U_{kl}^{i} \equiv U_{kl} [1 + m_{\rm e} (\Delta_{kl}^{\rm a} / M_{\rm a} + \Delta_{kl}^{\rm b} / M_{\rm b})]$$
(6)

and combining this with eqn (3), we obtain the expression

$$E^{i}(v,J) = \sum_{k} \sum_{l} U^{i}_{kl} [\mu_{i}^{-1/2}(v+\frac{1}{2})]^{k} [\mu_{i}^{-1}J(J+1)]^{l}$$
(7)

as an appropriate equation to which we fit experimental data when considering simultaneously several isotopically related molecules in an isolated ${}^{1}\Sigma$ state. The terms $\mu_{i}^{-1/2}(v+\frac{1}{2})$ and $\mu_{i}^{-1}J(J+1)$ are then regarded as mass-reduced quantum numbers.³¹ In practice, to determine the complete set of $\Delta_{kl}^{a,b}$ with statistical significance is not possible; in other words, many of the U_{kl}^{i} are essentially identical for the several isotopic molecules, especially as k or l increase beyond unity. Consequently the spectral data of several isotopic molecules can be simultaneously fitted to a set of U_{kl} in which only a few isotopically variant U_{kl}^{i} are retained. In the recent work³² on CO ($X^{1}\Sigma^{+}$), for instance, statistically significant determinations of only Δ_{10} , Δ_{20} , Δ_{30} and Δ_{01} were found.

In our work, the more reliable data for the isotopic molecules ${}^{1}\text{H}^{35}\text{Cl}$, ${}^{1}\text{H}^{37}\text{Cl}$, ${}^{2}\text{H}^{35}\text{Cl}$ and ${}^{2}\text{H}^{37}\text{Cl}$ have been fitted simultaneously according to a weighted least-squares criterion to eqn (7), for which isotopically variant U_{kl}^{i} were required in only the cases of U_{10} , U_{20} , U_{01} , U_{11} and U_{02} . In a subsequent correlated least-squares reduction based on eqn (6), Δ_{kl}^{Cl} values were found for only U_{01} and U_{10} . The parameters Δ_{20}^{H} , Δ_{11}^{H} and Δ_{02}^{H} are reported here for HCl for the first time.

Finally we have employed the equation

$$U_{kl} = U_{01} (2U_{01}/U_{10})^{k+2l-2} f_{kl}(a_i)$$
(8)

potential-energy function for HCl X $^{1}\Sigma^{+}$

in a further series of correlated, non-linear least-squares fits of the set of parameters U_{kl} and $\Delta_{kl}^{\mathrm{H,Cl}}$ in order to determine an optimum set of potential-energy coefficients a_i , $1 \le i \le 8$, that closely reproduce the numerical results according to the R.K.R. procedure. The functions $f_{kl}(a_i)$ are the leading terms (*i.e.* with Dunham corrections excluded) of the expressions generated by Dunham²⁵ and Sandeman³³ for the parameters Y_{kl} in terms of the potential-energy coefficients a_i .

COMPUTATIONAL METHOD AND RESULTS

The experimental wavenumbers of each band in our reduction procedure were first scrutinized in preliminary least-squares fits of the particular band. There were two purposes of these fits: first to identify and to reject subsequently any isolated lines with residuals anomalously large in relation to the estimated standard deviation of each band, and secondly to obtain reliable estimates of the standard deviation $\bar{\sigma}$ of each band. Such estimated values of $\bar{\sigma}$ were required to serve as weights $(\bar{\sigma}^{-2})$ for each segment of the data in the subsequent fit, according to weighted least-squares, of the entire data according to eqn (7). Because it was important that the estimates of $\bar{\sigma}$ should properly reflect the precision of experimental measurement of each band, the final fits of the individual bands were always performed with a reduced set of parameters $(\nu_0, B'_v, B''_v, D'_v, D''_v, \ldots)$ such that the parameters so estimated were all obtained with low standard errors. For bands with little rotational development, for instance, only ν_0 , B'_v and B''_v were fitted; all other necessary parameters were constrained at approximately correct values. This procedure avoids the problem of obtaining values of $\bar{\sigma}$ that are artificially too small from fits with an extended set of parameters, some of which would be determined with little, if any, statistical significance.

The results of the final series of preliminary fits are summarized in table 1. For each band, table 1 indicates the lines that were excluded, the rotational development $[J_m(P) \text{ and } J_m(R) \text{ are the maximum values of } J \text{ in the P- and R-branches, respec-}$ tively, of the lines retained for subsequent fitting], and the number (N) of lines retained. For those parts of the data with few lines, the method outlined above was inappropriate. For the pure rotational data for ${}^{1}H^{35}Cl$ in v = 2, for instance, $\bar{\sigma}$ was based on the results obtained for the corresponding transitions in v = 0 and v = 1. In the case of the millimetre-wave data, the $\bar{\sigma}$ values were generated from the standard deviations specified²⁰ for B_0 and D_0 .

Not all available data reviewed in the introduction are included in table 1. Thus, the pure rotational data of Akitt and Yardley,²² for instance, are much less precise than those of Deutsch,²³ and contribute essentially no useful additional information. Similarly, most data⁹ of Levy et al. have been superseded by more precise measurements, and the wavenumber precision of the 5 \leftarrow 0, 6 \leftarrow 0 and 7 \leftarrow 0 bands in ref. (15) and (16) is quite inferior to that obtained by Zughul.¹⁴

The simultaneous fit to eqn (7) of the data summarized in table 1 was performed in a stepwise manner similar to that outlined²⁷ for the method of stepwise merging. In the stepwise approach to fitting by weighted least-squares, the data of individual bands are progressively incorporated in a series of fits that lead to a steadily improving set of estimated U_{kl}^{\dagger} parameters. The weight matrix of each stage is composed of the dispersion matrix output from the preceding step, and a diagonal sub-matrix containing N equal elements given by $\bar{\sigma}^{-2}$ of the band being included. Not only is the stepwise approach far less exacting on computational resources than the equivalent procedure of a single-step, relatively large weighted fit of the entire set of data (here 896 measurements), but also it is sensitive to the location

TABLE 1.—SUMMARY OF LEAST-SQUARES FITS FOR INDIVIDUAL VIBRATIONAL-ROTATIONAL BANDS AND FOR PURE ROTATIONAL TRANSITIONS IN INDIVIDUAL LEVELS OF THE X $^{1}\Sigma^{+}$ STATES OF $^{1}H^{35}$ Cl, $^{1}H^{37}$ Cl, $^{2}H^{35}$ Cl and $^{2}H^{37}$ Cl a

| band/level | molecule | $\tilde{\sigma}/\mathrm{m}^{-1}$ | $J_{\rm m}({\rm P})$ | $J_{\rm m}({ m R})$ | N | excluded | ref. |
|--|--|--|---|--|--|--|---|
| 1-0 1-0 1-0 2-0 | ¹ H ³⁵ Cl ¹ H ³⁵ Cl ¹ H ³⁵ Cl ¹ H ³⁵ Cl | 0.110 0.051 0.223 0.201 | 29 2 29 23 | 34 13 27 19 | 39 16 48 41 | P(2, 7, 13), R(8, 14, 30) P(28, 30), R(0, 28, 30, 31) P(11, 19, 24–36) | 19 12 6 6 |
| 2-0 2-1 3-0 3-0 | ¹ H ³⁵ Cl ¹ H ³⁵ Cl ¹ H ³⁵ Cl ¹ H ³⁵ Cl | 0.009 0.095 0.349 0.125 | 12 27 8 9 | 12 27 10 8 | 25 45 15 18 | R(29) R(1, 5, 7, 11) | 11 19 6 12 |
| 3-1 3-2 4-0 4-2 | ¹ H ³⁵ Cl ¹ H ³⁵ Cl ¹ H ³⁵ Cl ¹ H ³⁵ Cl ¹ H ³⁵ Cl | 0.274 0.111 0.269 0.242 | 16 24 6 10 | 16 29 11 15 | 21 44 14 11 | R(0, 7) P(1, 2, 7), R(0) P(4) | 6 19 14 6 |
| 4-3 5-0 5-3 5-4 | ¹ H ³⁵ Cl ¹ H ³⁵ Cl ¹ H ³⁵ Cl ¹ H ³⁵ Cl | 0.113 0.697 0.350 0.125 | 21 7 7 15 | 22 9 0 17 | 34 15 3 21 | R(19, 23) R(0, 5) R(3) | 19 14 6 19 |
| $ \begin{array}{c} 6-0 \\ 6-5 \\ 7-0 \\ v = 0 \\ v = 0 \\ v = 1 \\ v = 2 \end{array} $ | ¹ H ³⁵ Cl ¹ H ³⁵ Cl | $\begin{array}{c} 0.390 \\ 0.309 \\ 0.861 \\ 1.3 \times 10^{-4} \\ 0.983 \\ 0.798 \\ 0.800 \end{array}$ | 7 0 5 | 10 6 9 1 40 26 25 | 13 3 14 1 16 8 2 | P(1, 2, 6), R(0, 4) R(9) P(6), R(4) | 14 19 14 20 23 23 23 |
| $ \begin{array}{r} 1-0\\ 1-0\\ 2-0\\ 3-0\\ 3-0\\ 4-0\\ 5-0\\ 6-0\\ 7-0\\ v=0\\ v=1\\ \end{array} $ | ¹ H ³⁷ Cl ¹ H ³⁷ Cl | $\begin{array}{c} 0.059\\ 0.848\\ 0.016\\ 0.929\\ 0.028\\ 0.389\\ 0.508\\ 0.696\\ 0.949\\ 2.144\\ 1.3 \times 10^{-4}\\ 0.800\end{array}$ | 2 19 11 13 7 8 7 6 6 5 | 12 20 11 11 5 9 10 8 9 8 1 20 | 15 25 22 22 12 17 17 14 15 14 1 1 | R(21, 22) R(10) P(13), R(13) R(0) R(5) R(4) | 12 7 11 8 12 9 14 14 14 14 20 23 |
| $ \begin{array}{r} 1-0\\ 2-0\\ 2-1\\ 3-0\\ 3-0\\ 3-2\\ 4-3\\ 5-4\\ v=0\\ v=0\\ v=0\\ \end{array} $ | ² H ³⁵ Cl ² H ³⁵ Cl | $\begin{array}{c} 0.208\\ 0.024\\ 0.201\\ 2.9\\ 0.054\\ 0.336\\ 2.9\\ 2.9\\ 2.9\\ 2.9\\ 1.0\times10^{-4}\\ 3.7\times10^{-4} \end{array}$ | 8 15 15 9 11 16 11 11 9 | 16 16 14 0 11 16 0 0 0 0 1 1 | 18 28 28 5 22 9 8 6 4 1 1 | P(6), R(14, 15) R(5) R(15) | 5 12 5 23 12 10 23 23 20 20 |
| $ \begin{array}{r} 1-0\\ 2-0\\ 2-1\\ 3-0\\ 3-0\\ 3-2\\ 4-3\\ v=0\\ v=0\\ \end{array} $ | ² H ³⁷ Cl ² H ³⁷ Cl ² H ³⁷ Cl ² H ³⁷ Cl ³ H ³⁷ Cl ² H ³⁷ Cl | $\begin{array}{c} 1.254\\ 0.051\\ 0.817\\ 2.9\\ 0.134\\ 0.443\\ 2.9\\ 2.9\\ 1.1 \times 10^{-4}\\ 3.8 \times 10^{-4} \end{array}$ | 15 14 12 8 8 14 8 8 | 17 15 15 0 6 13 0 0 0 0 1 | 29 28 27 4 12 15 4 3 1 1 | P(4) R(12, 14) P(13) R(1) P(15), R(14) | 8 12 8 23 12 10 23 23 20 20 |

^a σ is the estimated standard deviation; $J_m(P)$ and $J_m(R)$ indicate rotational developments (see text); N is the number of lines fitted; lines omitted from the fits are listed in the column headed 'excluded'.

of serious relative systematic errors within the data. In the present work, for instance, we found the absolute wavenumbers obtained by Deutsch²³ and by Zughul¹⁴ to be subject to appreciable systematic error in relation to the other data. However, we fortunately discovered that the unduly large variance of the weighted fit, and hence also the associated contamination of the fitted parameters due to such systematic error, could be virtually eliminated by assuming that the wavenum-ber measurements^{14,23} were subject to constant displacements δ from their true values. The parameters δ could then be included in the set of parameters to be fitted; as later shown, the fitted values of δ are ca. -1.9 and -5.6 m⁻¹ for the two data sets, respectively.

In a preliminary, weighted least-squares fit of the kind discussed above, but restricted to the relatively extensive data of ¹H³⁵Cl alone, we included sufficient parameters in the expansion of eqn (7) that no significant contribution to the variance of the fit would result from an inadequate model owing to premature truncation of the summations. Some higher-order parameters such as U_{23} and U_{14} were consequently poorly determined; all U_{k5} were set to zero. Nevertheless the set of potential-energy coefficients a_i , $1 \le i \le 8$, obtained from the preliminary values of U_{k0} , $1 \le k \le 5$, and U_{k1} , $0 \le k \le 4$, were reliable enough to permit useful calculations of U_{k4} and U_{k5} for use as constraints in the final stage of fitting the data of all four isotopic molecules. The results of the latter fit, together with the constrained values of U_{kl} , are listed in the column labelled fit A in table 2. The estimated variance of the fit is given by $\bar{\sigma}_{w}^{2} = 1.373^{2}$, a value that by its significant deviation from unity indicates the presence of residual relative systematic error within the data. For the numerous degrees of freedom in the fit, $f_w = 896 - 28 = 868$, $\bar{\sigma}_{w}^{2}$ follows a narrow distribution with a mean of unity for data subject to only random error of measurement.³⁴

In order to assess further the influence of systematic error, especially for the purpose of obtaining reliable standard errors for the fitted parameters, we consider the results of Albritton *et al.*³⁴ and $Coxon^{27}$ for the alternative, but equivalent, fitting procedure known as merging. In this method, estimates of parameters from separate segments of the data are merged in a correlated least-squares fit so that the same final single-valued estimates are obtained as those found from the weighted fit. Unlike the ill-defined distribution for $\bar{\sigma}_{w}^{2}$, the variance $\bar{\sigma}_{m}^{2}$ of a merged fit follows a well defined distribution (χ^2/f_m) for data subject to only random, normally distributed errors of measurement; even in the presence of moderate systematic error, as in the present case, reliable estimates of standard errors can still be obtained from the experimental value of $\bar{\sigma}_m$. The relationship³⁴ between $\bar{\sigma}_w^2$ and $\bar{\sigma}_{\rm m}^2$ is

$$f_{\rm m}(\bar{\sigma}_{\rm m}^2 - 1) = f_{\rm w}(\bar{\sigma}_{\rm w}^2 - 1). \tag{9}$$

The application of eqn (9) requires an estimate of f_m , the degrees of freedom for the equivalent merge fit. We estimate that for the data in table 1 ca. 250 parameters would be obtained from fits of the individual bands or of small groups of bands with sparse data; on this basis the variance of the merge fit would be $\bar{\sigma}_m^2 = 2.118^2$. In accord with the earlier comments, this value lies well outside the 95% confidence limits for the $\chi^2/222$ distribution, and implies²⁷ that standard errors $\bar{\sigma}_i$ of the fitted parameters should be obtained as $\bar{\sigma}_m \bar{V}_{ii}^{1/2}$; \bar{V} is the dispersion-matrix output from the weighted least-squares fit. This procedure was adopted in obtaining the results in table 2.

Also given in table 2, the results of a second fit B were obtained when the mass-dependent parameters U_{kl}^{i} of fit A were reduced to the mass-invariant set

| | A ^b | | B ^b |
|--|------------------------------|---------------------------|------------------------------|
| $U_{10}(^{1}\text{H}^{35}\text{Cl}) = 2$ | 296 021.586(267) | $U_{10} = 2$ | 96 031.315(212) |
| $U_{10}(^{1}\text{H}^{37}\text{Cl}) = 2$ | 96 021.553(267) | $\Delta_{10}^{H} =$ | -0.064 12(90) |
| $U_{10}(^{2}\text{H}^{35}\text{Cl}) = 2$ | .96 026.743(225) | $\Delta_{10}^{Cl} =$ | 0.129 3(154) |
| $U_{10}(^{2}\text{H}^{37}\text{Cl}) = 2$ | 96 026.718(225) | | |
| $U_{20}(^{1}\text{HCl}) =$ | -5 168.347 5(2216) | $U_{20} = -$ | -5 169.434 7(2021) |
| $U_{20}(^{2}\text{HCl}) =$ | -5 168.890(210) | $\Delta_{20}^{H} =$ | -0.386 9(174) |
| $U_{30} =$ | 19.158 0(779) | $U_{30} =$ | 19.157 6(779) |
| $U_{40} =$ | -0.639 63(1208) | $U_{40} =$ | -0.639 59(1209) |
| $U_{50} =$ | -0.040 12(68) | $U_{50} =$ | -0.040 12(68) |
| $U_{01}(^{1}\text{H}^{35}\text{Cl}) =$ | 1 037.709 79(81) | $U_{01} =$ | 1037.639 97(272) |
| $U_{01}({}^{1}\mathrm{H}{}^{37}\mathrm{Cl}) =$ | 1 037.709 96(81) | $\Delta_{01}^{H} =$ | 0.131 5(10) |
| $U_{01}(^{2}\mathrm{H}^{35}\mathrm{Cl}) =$ | 1 037.672 57(61) | $\Delta_{01}^{Cl} =$ | -0.278(168) |
| $U_{01}(^{2}\mathrm{H}^{37}\mathrm{Cl}) =$ | 1 037.672 95(61) | | |
| $U_{11}(^{1}\text{HCl}) =$ | -29.758 85(225) | $U_{11} =$ | -29.751 52(197) |
| $U_{11}(^{2}\text{HCl}) =$ | -29.755 19(210) | $\Delta_{11}^{H} =$ | 0.451(29) |
| U ₂₁ = | 0.151 555(1540) | $U_{21} =$ | 0.151 544(1540) |
| $U_{31} =$ | $-6.105(386) \times 10^{-3}$ | $U_{31} =$ | $-6.103(386) \times 10^{-3}$ |
| $U_{41} =$ | $-5.117(309) \times 10^{-4}$ | $U_{41} =$ | $-5.119(309) \times 10^{-4}$ |
| $U_{02}(^{1}\text{HCl}) =$ | -0.051 0143(26) | $U_{02} =$ | -0.050 997 6(113) |
| $U_{02}(^{2}\text{HCl}) =$ | -0.051 0057(60) | $\Delta_{02}^{H} =$ | 0.60(41) |
| $U_{12} =$ | $6.8723(655) \times 10^{-4}$ | $U_{12} =$ | $6.8717(655) \times 10^{-4}$ |
| $U_{22} =$ | $-2.614(457) \times 10^{-5}$ | $U_{22} =$ | $-2.610(457) \times 10^{-5}$ |
| $U_{32} =$ | $-7.31(1108) \times 10^{-7}$ | $U_{32} =$ | $-7.39(1108) \times 10^{-7}$ |
| $U_{42} =$ | $-9.84(792) \times 10^{-8}$ | $U_{42} =$ | $-9.80(792) \times 10^{-8}$ |
| $U_{03} =$ | $1.5958(21) \times 10^{-6}$ | $U_{03} =$ | $1.5957(21) \times 10^{-6}$ |
| $U_{13} =$ | $-5.252(435) \times 10^{-8}$ | $U_{13} =$ | $-5.248(435) \times 10^{-8}$ |
| U ₂₃ = | $2.68(278) \times 10^{-9}$ | $U_{23} =$ | $2.65(278) \times 10^{-9}$ |
| $U_{33} =$ | $-1.551(474) \times 10^{-9}$ | $U_{33} =$ | $-1.547(474) \times 10^{-9}$ |
| δ (Deutsch) = | -1.80(13) | δ (Deutsch) = | -1.88(13) |
| $\delta(\text{Zughul}) =$ | -5.6(11) | $\delta(\text{Zughul}) =$ | -5.6(11) |

TABLE 2.—MASS-REDUCED (A) AND MASS-INVARIANT (B) PARAMETERS FOR THE X ¹ Σ ⁺ state of HCl from weighted least-squares fits^a

^a In this table and table 3, units are as follows: U_{kl} , m⁻¹ amu^{(k+2l)/2}; δ , m⁻¹; Δ , dimensionless. Atomic masses used are: ¹H = 1.007 825 036, ²H = 2.014 101 795, ³⁵Cl = 34.968 853 59, ³⁷Cl = 36.965 903 04 amu. $m_e = 5.485 802 3 \times 10^{-4}$ amu. 1 amu = 1.660 565 5×10^{-27} kg. Values in parentheses are estimated (one) standard errors in units of the last significant digits quoted. ^b Parameters were obtained with the constraints: $U_{04} = -7.8275 \times 10^{-11}$, $U_{14} = -2.1106 \times 10^{-12}$, $U_{24} = -5.310 \times 10^{-13}$, $U_{34} = 1.007 \times 10^{-13}$, $U_{05} = 2.825 \times 10^{-15}$.

 $(U_{kl} \text{ and } \Delta_{kl}^{\text{H,Cl}})$ according to eqn (6). The variances of fits A and B are essentially identical, and the fitted values of those parameters assumed at the outset to be mass-invariant differ negligibly between the two fits. The parameters of both fits thus reproduce the data equally well; in fact the value of $\bar{\sigma}_w$ indicates that the root-mean-square values of the residuals between the observed and calculated wavenumbers are on average *ca.* 37% larger than the standard deviations given in table 1.

DISCUSSION

The principal result of the fitting by weighted least-squares described in the preceding sections is the set of mass-invariant parameters, the mass-reduced energy

coefficients U_{kl} and the associated elemental mass coefficients $\Delta_{kl}^{H,Cl}$ given as fit B in table 2. The present work is a significant extension of, and improvement upon, the results of Guelachvili *et al.*,¹² which were concerned with states of HCl $(X^{1}\Sigma^{+})$ in an energy range only about half that represented by the parameters in table 2. We have been able to obtain the first estimates of $\Delta_{20}^{\rm H}$, $\Delta_{11}^{\rm H}$ and $\Delta_{02}^{\rm H}$, and these will be of interest in future theoretical interpretations of such mass coefficients.²⁶ Moreover, our parameters reproduce the entire set of wavenumber data considerably better than is found with the set of Guelachvili et al.¹² for a more limited amount of data. This effect is probably due, at least in part, to the different weighting procedure that we have adopted. As earlier emphasized, we have attempted to obtain reliable estimates of the actual precision of each segment of the data for use in determining weighting factors. Guelachvili et al.¹² on the other hand provide no detail on the choice of weight factors for the earlier data, and assume specific precisions of $2.5 \times 10^{-7} \nu$ and $4.0 \times 10^{-7} \nu$ for the two distinct sets of infrared data and $10^{-7} \nu$ for the microwave data. Thus for the 2–0 bands of ²H³⁵Cl and ²H³⁷Cl, for instance, the assumed¹² precision of *ca.* 0.1 m⁻¹ can be compared with the values in table 1 of 0.024 and 0.051 m^{-1} , respectively. When we back-calculate the 2-0 band of ²H³⁵Cl, for instance, with the parameters of 2. the root-mean-square deviation of the residuals is only table ca. 0.033 m^{-1} , ca. 40% larger than the estimated precision, but in accord with the expected average differential of 37% based on σ_{w} . In contrast, the published parameters¹² yield a root-mean-square deviation of 0.113 m⁻¹, more than three times as large as our value, but still considerably better than expected from $\bar{\sigma}_{w} = 1.9^{12}$ Å notable point in this regard is the comparison that Guelachvili et al^{12} make between their value of $\bar{\sigma}_{w} = 1.9$ for the simultaneous fit of the data for all four isotopic molecules with the significantly smaller values found for the fits for each separate isotopic molecule; in fact the values $\sigma_{\rm w} = 1.0$ found for ¹H³⁵Cl and ${}^{1}\text{H}^{37}\text{Cl}$, which would imply the absence of any systematic error, are fortuitously a consequence of the conservative weight factors adopted.

As mentioned in the introduction, one objective of this study was to obtain an optimum truncated set of potential-energy coefficients a_i for HCl independent of mass. We considered various approaches, all of which involved correlated nonlinear least-squares fits to the parameter set B in table 2. Coefficient matrices were generated from the $f_{kl}(a_i)$ factors of eqn (8) using the expressions of ref. (29). In an initial run, the fit performed was a transformation of the eight parameters U_{k0} , $2 \le k \le 5$, and U_{k1} , $1 \le k \le 4$, to the set a_i , $1 \le i \le 8$, leaving U_{10} and U_{01} fixed at their specified values because by definition no Dunham correction terms are applicable. All the remaining 18 parameters of fit B in table 2 retained their definitions, and were allowed to vary in the least-squares sense. The results of this fit are depicted in fig. 1, which shows comparisons for the limb R_{max} between the R.K.R. potential-energy points and the two potential-energy curves generated from different sets of coefficients a_i. Both curves reproduce closely the R.K.R. points for the limb R_{\min} : the maximum discrepancy is only 250 m⁻¹ for the turning point at v = 7, and would not be visible on the scale of the figure. For the limb R_{max} , however, large discrepancies occur: for the fit described above, agreement is tolerable for R_{max} for $v \leq 3$ (the discrepancy is *ca*. 10^3 m^{-1} at v = 3), but at larger values of R the curve diverges rapidly from the R.K.R. points. In the second fit, the potential-energy coefficients a_i were simultaneously determined from all U_{kl} values in fit B of table 2, except the poorly determined parameters U_{23} and U_{33} . Although the variance of this fit, $\bar{\sigma}^2 = 6.646^2$ with f = 7 degrees of freedom, does not substantially affect that of the equivalent single-step weighted fit of the



FIG. 1.—Dependence of potential energy V(R) on internuclear separation R for R.K.R. points (circles) and Dunham functions (broken curves) fitted with 8 or 16 U_{kl} and labelled A and B, respectively.

wavenumber data to the same parameters ($\bar{\sigma}_w = 1.491$, cf. $\bar{\sigma}_w = 1.373$ for fit B in table 2), the fitted coefficients a_i are even less successful in reproducing the R.K.R. points than those obtained from the transformation of the fewer U_{kl} . Both fits are characterised by poorly determined and greatly different values of coefficients a_7 and a_8 , which are largely responsible for the discrepancies in fig. 1.

The sensitivity of a_7 and a_8 to the particular set of U_{kl} used is undoubtedly due to the effects of truncation.²⁸ U_{50} and U_{42} are functions of a_i , $1 \le i \le 8$, whereas U_{41} depends on a_i , $1 \le i \le 7$; these three U_{kl} are terminal parameters in the truncated set of U_{kl} , and hence the least reliable parameters. We therefore decided that a preferable approach would be a fit in which the U_{kl} parameters most affected by truncation were ignored in the determination of the a_i ; in addition to the three specified U_{kl} , we also neglected U_{32} . Clearly there are then no parameters left that would lead to a determination of a_7 and a_8 . We surmounted this problem in a final fit by introducing the R.K.R. points of R_{max} for v = 6 and v = 7 as parallel, uncorrelated input data, which could hence be reproduced closely by the fitted set of coefficients a_i , $1 \le i \le 8$. This set and the remaining 15 parameters that were allowed to vary are listed in the first column of table 3; the variance of the fit was $\bar{\sigma}^2 = 3.858^2$ with f = 7 degrees of freedom, leading to an overall $\bar{\sigma}_w = 1.410$. This result implies that the parameters U_{kl} given in the second column of table 3, and which are calculated where appropriate from the fitted values in the first column, can reproduce the wavenumber measurements almost as well as those of table 2. An interesting result of the fit is that Δ_{02}^{H} in table 3 is determined with great significance, whereas its determination according to table 2 is barely significant; this effect is due to the exact determination of U_{02} by the pair U_{10} and U_{01} , thereby breaking the otherwise strong correlation between U_{02} and Δ_{02}^{H} .

In the third column of table 3 we list values calculated for those U_{kl} that were either left free, or constrained, in the fit of the first column; as for the second column, the calculations use the fitted values of U_{10} , U_{01} and a_i , $1 \le i \le 8$, and employ the expressions of ref. (29). Although the fitted values of U_{50} , U_{41} , U_{32} ,

| 1354 POTENTIAL-ENERGY FUNCTION | on for HCl <i>X</i> | $\zeta^{-1}\Sigma^{+}$ |
|--------------------------------|---------------------|------------------------|
|--------------------------------|---------------------|------------------------|

| | fitted | back | -calculated | calculated | | |
|---------------------------|------------------------------|--|-----------------------------|---|--|--|
| $U_{10} = 2$ | 296031.403(208) | $U_{10} = 2$ | 96 031.403 | | | |
| $U_{01} =$ | 1037.63962(273) | $37.63962(273) \qquad U_{20} = -5\ 169.525\ 5$ | | | | |
| | | $U_{30} =$ | 19.110 | | | |
| $a_1 =$ | -2.363 3725(352) | $U_{40} =$ | -0.643 93 | | | |
| $a_2 =$ | 3.660 5756(1938) | $U_{50} =$ | -0.039 95 | $U_{50} = -0.0454(71)$ | | |
| $a_3 =$ | -4.749 210(1326) | $U_{01} =$ | 1037.639 62 | | | |
| $a_4 =$ | 5.452 896(9948) | $U_{11} =$ | -29.752 34 | | | |
| $a_5 =$ | -5.515 98(3199) | $U_{21} =$ | 0.152 354 | | | |
| $a_6 =$ | 4.284 0(1274) | $U_{31} =$ | -6.388×10^{-3} | | | |
| $a_7 =$ | -1.726 2(4152) | $U_{41} =$ | -4.792×10^{-4} | $U_{41} = -3.82(56) \times 10^{-4}$ | | |
| $a_8 =$ | -0.026 7(3918) | $U_{02} =$ | -5.09946×10^{-2} | | | |
| | | $U_{12} =$ | 6.8518×10^{-4} | | | |
| $U_{50} =$ | -0.039 95(70) | $U_{22} =$ | -2.494×10^{-5} | _ | | |
| $U_{41} =$ | $-4.792(144) \times 10^{-4}$ | $U_{32} =$ | -6.16×10^{-7} | $U_{32} = -10(8) \times 10^{-7}$ | | |
| U ₃₂ = | $-6.16(99) \times 10^{-7}$ | $U_{42} =$ | -1.61×10^{-7} | $U_{42} = -1.98(26) \times 10^{-7}$ | | |
| $U_{42} =$ | $-1.61(13) \times 10^{-7}$ | $U_{03} =$ | 1.5955×10^{-6} | | | |
| | 0 | $U_{13} =$ | -4.585×10^{-8} | | | |
| $U_{23} =$ | $-2.071(158) \times 10^{-9}$ | $U_{23} =$ | -2.071×10^{-9} | $U_{23} = 1.64(13) \times 10^{-9}$ | | |
| $U_{33} =$ | $-7.87(45) \times 10^{-10}$ | $U_{33} =$ | -7.87×10^{-10} | $U_{33} = -4.85(75) \times 10^{-10}$ | | |
| | | $U_{04} =$ | $[-7.8275 \times 10^{-11}]$ | $U_{04} = -7.8395(19) \times 10^{-11}$ | | |
| $\Delta_{10}^{H} =$ | -0.063 82(88) | $U_{14} =$ | $[-2.1106 \times 10^{-12}]$ | $U_{14} = -2.1375(776) \times 10^{-12}$ | | |
| $\Delta_{10}^{Cl} =$ | 0.128 0(158) | $U_{24} =$ | $[-5.310 \times 10^{-13}]$ | $U_{24} = -4.055(564) \times 10^{-13}$ | | |
| $\Delta_{20}^{H} =$ | -0.382 4(174) | $U_{34} =$ | $[1.007 \times 10^{-13}]$ | $U_{34} = -0.808(66) \times 10^{-13}$ | | |
| $\Delta_{01}^{H} =$ | 0.132 0(7) | $U_{05} =$ | $[2.825 \times 10^{-15}]$ | $U_{05} = 2.8804(83) \times 10^{-15}$ | | |
| $\Delta_{01}^{CI} =$ | -0.250(17) | $U_{15} =$ | [0.0] | $U_{15} = -5.4(15) \times 10^{-17}$ | | |
| $\Delta_{11}^{H} =$ | 0.462(19) | $U_{25} =$ | [0.0] | $U_{25} = -1.08(14) \times 10^{-16}$ | | |
| $\Delta_{02}^{H} =$ | 0.74(4) | $U_{06} =$ | [0.0] | $U_{06} = 2.488(20) \times 10^{-19}$ | | |
| | | $U_{16} =$ | [0.0] | $U_{16} = -5.30(56) \times 10^{-20}$ | | |
| δ (Deutsch) = | -1.89(13) | $U_{07} =$ | [0.0] | $U_{07} = 9.75(24) \times 10^{-24}$ | | |
| $\delta(\text{Zughul}) =$ | -5.6(11) | $U_{08} =$ | [0.0] | $U_{08} = -1.58(7) \times 10^{-27}$ | | |
| | | $U_{09} =$ | [0.0] | $U_{09} = 1.12(18) \times 10^{-32}$ | | |

TABLE 3.—FITTED POTENTIAL-ENERGY COEFFICIENTS, U_{kl} and Δ_{kl} parameters, AND CALCULATED U_{kl} parameters for the X $^{1}\Sigma$ state of HCl a

^a Units are as given in footnote of table 2. Entries in square brackets denote constrained values of parameters in the weighted least-squares fit.

 U_{42} , U_{23} and U_{33} are expected to differ from the calculated values, because of the truncation effects, the agreement is still good, mostly within two standard errors. Except for U_{34} , the calculated values of U_{05} and the U_{k4} set differ little from those adopted as constraints in the fits. Finally we also list calculated values of parameters of higher order; these may prove useful in future work with more precise or rotationally extensive data.

Differences between the potential-energy curve generated by the parameters a_i in table 3 and the R.K.R. points are too small to be discernible in fig. 1. The overall agreement is illustrated by the plot in fig. 2, which shows the variation of the difference between the two sets of data as a function of internuclear separation **R.** Fig. 2 shows a remarkable correspondence between the R.K.R. points and Dunham curve over the entire range of R to which the data are sensitive. Of course, the Dunham potential-energy curve outside this range cannot be expected to maintain any reliability.

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FIG. 2.—Dependence of difference of potential-energy functions, $\Delta V(R) = V_{R.K.R.}(R) - V_{Dunham}(R)$, on internuclear separation R.

The R.K.R. points for HCl $(X^{1}\Sigma^{+})$ listed in table 4 are calculated for a hypothetical isotopic molecule with unit reduced mass. As emphasised by Watson,²⁶ this calculation is performed with the simple unmodified approach,²⁴ in which integration for the Born-Oppenheimer potential-energy function is performed above the limit of $v = -\frac{1}{2}$ exactly. The R.K.R. points were calculated both with a program recently developed³⁶ at Dalhousie University and with Tellinghuisen's program;³⁷ agreement was obtained within 10^{-16} m.

As demonstrations of the quality of our estimates of parameters, and also to make available those data previously unpublished, we list in tables 5 and 6 the wavenumbers and residuals of the bands measured by Clayton¹⁹ and Zughul, respectively. Although the residuals clearly indicate small systematic trends, as expected from the earlier discussion, the root-mean-square values are found on average to be *ca.* 1.4 times the standard deviations listed in table 1. As further checks of the reliability of the mass-scaling factors $\Delta_{kl}^{H,Cl}$ listed in table 3, we compare calculated values of the frequencies for $J = 1 \leftarrow J = 0$ in v = 0 for ${}^{3}H^{35}Cl$ and ${}^{3}H^{37}Cl$ with the experimental measurements of Burrus *et al.*²¹ (No data of ³HCl were included in the parameter fits.) The calculated values are 222.143 893 and 222.195 179 GHz; both results lie within the error limits of the experimental values, ²¹ 222.143 $78 \pm 4 \times 10^{-4}$ GHz for ³H³⁵Cl and 222.195 $40 \pm 4 \times 10^{-4}$ GHz for ${}^{3}\text{H}^{37}\text{Cl}$. Similarly for the fundamental vibrational-rotational bands of ${}^{3}\text{HCl}$, the wavenumbers calculated on the basis of parameters in table 3 are greater by $27 \pm 16 \text{ m}^{-1}$ for ${}^{3}\text{H}^{35}\text{Cl}$ and $30.7 \pm 12.5 \text{ m}^{-1}$ for ${}^{3}\text{H}^{37}\text{Cl}$ than those measured with a spectral slit width of ca. 100 m⁻¹. However, the calibration spectra³⁸ of ²HBr used for the ³HCl measurements³⁹ also have a systematic deviation of ca. 24 m⁻¹ from modern data;⁴⁰ after we take account of this correction, the agreement between calculated and observed wavenumbers is well within the experimental error specified³⁹ by Jones and Robinson.

After completion of the analysis of the data sets listed in table 1, further data on ${}^{1}\text{H}{}^{37}\text{Cl}$ became available.¹⁹ These data are also incorporated in table 5. For these 189 lines, the average deviation is $-0.088 \pm 0.28 \text{ m}^{-1}$ and the r.m.s. error is

| v | G_v/m^{-1} | B_v/m^{-1} | $\frac{R_{min}(v)}{10^{-10}}$ m | $\frac{R_{max}(v)}{10^{-10}}$ m |
|---|-----------------------|--------------|---------------------------------|---------------------------------|
| 0 | 146 725.68 | 1022.8007 | 1.177 730 | 1.392 736 |
| 1 | 432 476.88 | 993.3299 | 1.117 949 | 1.495 931 |
| 2 | 708 039.78 | 964.0924 | 1.081 552 | 1.577 014 |
| 3 | 973 488.42 | 935.0269 | 1.054 582 | 1.650 064 |
| 4 | 1228 869.4 | 906.0606 | 1.033 040 | 1.719 226 |
| 5 | 1474 197.2 | 877.1091 | 1.015 122 | 1.786 484 |
| 6 | 1709 449.0 | 848.0765 | 0.999 835 | 1.853 047 |
| 7 | 1934 560.4 | 818.8556 | 0.986 566 | 1.919 791 |

TABLE 4.—BORN-OPPENHEIMER POTENTIAL-ENERGY OF HCl $(X \ ^{1}\Sigma^{+})$ (R.K.R. METHOD)^a

^a The G_v and B_v values refer to a hypothetical isotopic molecule of HCl with $\mu = 1.000\ 000$ amu. The usual Dunham correction Y_{00} in a R.K.R. calculation is set to zero. Values of the physical constants were taken from ref. (35).

Table 5.—Vacuum wavenumbers 19 and residuals (both in $m^{-1})$ for the Δv = 1 sequence of HCl $^{\alpha}$

| | | $1 \rightarrow 0$ band | ¹ H ³⁵ Cl | | | $1 \rightarrow 0$ band | ¹ H ³⁷ Cl | |
|----|-----------------------|---------------------------|---------------------------------|-------|------------------------|---------------------------|---------------------------------|-------|
| J | P (<i>J</i>) | Δ | R(J) | Δ | P (J)* | Δ | R(<i>J</i>)* | Δ |
| 0 | | | | | | _ | _ | |
| 1 | | | | | 286 302.44 | 0.05 | | |
| 2 | 284 362.47* | -0.02 | | | 284 157.97 | -0.33 | | |
| 3 | 282 156.55 | -0.33 | | | 281 955.64 | -0.44 | | |
| 4 | | _ | | | | _ | | |
| 5 | | | 299 804.25 | -0.43 | | | 299 578.19 | -0.09 |
| 6 | | | | | | | 301 212.27 | -0.50 |
| 7 | 272 777.33* | -0.67 | | | 272 591.67 | -0.35 | 302 777.95 | -0.32 |
| 8 | 270 300.28 | -0.50 | 304 505.20* | -0.65 | 270 118.35 | -0.44 | 304 273.03 | -0.63 |
| 9 | 267 772.80 | -0.45 | 305 931.14 | -0.52 | 267 595.09 | -0.26 | 305 697.38 | -0.48 |
| 10 | 265 196.30 | -0.44 | 307 284.66 | -0.38 | 265 022.59 | -0.45 | 307 049.68 | -0.13 |
| 11 | — | | 308 564.82 | -0.14 | | | 308 328.28 | -0.21 |
| 12 | | | 309 770.27 | -0.16 | 259 737.14 | -0.05 | 309 532.67 | -0.20 |
| 13 | 257 186.89* | -0.02 | 310 900.27 | -0.17 | 257 026.26 | -0.11 | 310 661.70 | -0.29 |
| 14 | 254 427.79 | -0.26 | 311 954.12* | 0.08 | 254 271.36 | -0.71 | 311 714.60 | -0.28 |
| 15 | 251 626.67 | -0.33 | 312 930.11 | -0.20 | 251 475.35 | -0.31 | 312 690.42 | -0.20 |
| 16 | 248 784.90 | -0.20 | 313 828.33 | 0.00 | 248 638.27 | -0.21 | | |
| 17 | 245 903.57 | -0.13 | 314 647.10 | -0.13 | 245 761.80 | -0.08 | 314 407.03 | -0.03 |
| 18 | 242 984.03 | -0.11 | 315 386.16 | 0.00 | 242 847.14 | -0.04 | 315 145.97 | -0.06 |
| 19 | 240 027,55 | -0.20 | 316 044.13 | -0.17 | 239 895.56 | -0.16 | 315 804.39 | -0.02 |
| 20 | 237 035.66 | -0.20 | 316 620.94 | 0.09 | 236 908.97 | 0.15 | 316 381.40 | 0.01 |
| 21 | 234 009.58 | -0.20 | 317 114.90 | -0.13 | 233 887.64 | -0.15 | 316 876.07 | -0.14 |
| 22 | 230 950.56 | -0.25 | 317 525.86 | -0.24 | 230 833.70 | -0.22 | 317 287.87 | -0.25 |
| 23 | 227 860.16 | -0.07 | | | 227 748.43 | -0.07 | 317 616.11 | -0.29 |
| 24 | 224 739.22 | -0.10 | | | 224 632.71 | -0.08 | | |
| 25 | _ | | 318 253.46 | -0.15 | 221 488.06 | 0.01 | | |
| 26 | 218 411,48 | -0.03 | 318 324.95 | -0.34 | 218 315.60 | 0.09 | | |
| 27 | 215 207.22 | 0.17 | 318 310.18 | -0.32 | 215 116.62 | 0.25 | 318 079.93 | 0.18 |
| 28 | | | 318208.37 | -0.26 | 211 891.89 | 0.05 | 317 979.84 | -0.11 |
| 29 | 208 723.20 | 0.19 | | | 208 643.32 | 0.24 | 317 792.36 | -0.34 |
| 30 | | | 317 741.53* | 0.21 | | | 317 517.84 | 0.43 |
| 31 | _ | | 317 374.63 | -0.08 | | | 317 153.07 | -0.46 |
| 32 | | | 316 918.82 | 0.05 | | _ | | |
| 33 | _ | | _ | | | | 316 158.75 | 0.90 |
| 34 | | | 315 736.54 | -0.19 | | | | |

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|----|-----------------------|---------------------------|---------------------------------|-------|------------------------|------------------------|---------------------------------|-------|
| | | $2 \rightarrow 1$ band | ¹ H ³⁵ Cl | | | $2 \rightarrow 1$ band | ¹ H ³⁷ Cl | |
| J | P (<i>J</i>) | Δ | $\mathbf{R}(J)$ | Δ | P (<i>J</i>)* | Δ | R(J)* | Δ |
| 0 | _ | | 280 167.30 | -0.07 | | | 279 969.40 | -0.14 |
| 1 | 276 173.57 | -0.06 | | | 275 981.56 | -0.10 | 281 871.87 | -0.10 |
| 2 | 274 087.35 | -0.18 | 283 914.82 | -0.09 | 273 898.51 | -0.19 | | |
| 3 | 271 943.66 | 0.02 | 285 693.31 | -0.01 | 271 758.01 | -0.05 | 285 487.66 | -0.10 |
| 4 | 269 743.13 | -0.09 | 287 406.45 | -0.11 | 269 560.91 | -0.12 | 287 198.63 | -0.09 |
| 5 | 267 487.61 | 0.04 | 289 053.38 | -0.08 | 267 308.76 | -0.12 | 288 843.36 | -0.14 |
| 6 | | | | | 265 002.59 | -0.31 | 290 420.67 | -0.28 |
| 7 | 262 815.82 | 0.08 | 292 143.56 | -0.14 | 262 644.52 | 0.11 | 291 929.74 | -0.22 |
| 8 | 260 402.13 | -0.06 | 293 584.72 | -0.07 | 260 234.61 | -0.09 | 293 369.20 | -0.20 |
| 9 | 257 938.58 | -0.05 | 294 954.98 | -0.09 | 257 775.08 | -0.01 | 294 738.22 | 0.01 |
| 10 | | | 296 253.51 | 0.02 | 255 266.49 | -0.40 | 296 035.29 | -0.03 |
| 11 | 252 866.50 | -0.27 | 297 478.83 | -0.16 | 252 711.23 | -0.21 | 297 259.71 | 0.02 |
| 12 | 250 260.98 | -0.15 | 298 630.34 | -0.22 | 250 109.88 | -0.15 | 298 410.17 | -0.13 |
| 13 | 247 610.65 | -0.13 | _ | | 247 464.58 | 0.57 | 299 486.09 | -0.08 |
| 14 | 244 917.07 | 0.04 | 300 707.74 | -0.22 | 244 774.63 | -0.05 | 300 486.16 | -0.17 |
| 15 | 242 181.09 | -0.13 | 301 631.79 | -0.07 | 242 043.14 | -0.22 | | |
| 16 | | — | | | 239 271.25 | -0.12 | 302 255.59 | -0.14 |
| 17 | 236 588.20 | -0.43 | 303 245.39 | -0.07 | 236 459.43 | -0.57 | | |
| 18 | | | 303 933.55 | 0.17 | | | 303 711.34 | 0.11 |
| 19 | 230 843.19 | -0.24 | _ | — | 230 724.10 | -0.20 | 304 319.21 | 0.11 |
| 20 | 227 916.55 | -0.18 | 305 067.14 | -0.03 | 227 802.32 | -0.23 | 304 845.88 | -0.05 |
| 21 | 224 955.77 | -0.14 | 305 511.41 | 0.00 | 224 846.37 | -0.26 | 305 291.18 | 0.27 |
| 22 | 221 961.83 | -0.09 | 305 872.84 | 0.03 | 221 857.31 | -0.20 | 305 653.52 | 0.27 |
| 23 | 218 936.02 | -0.09 | 306 150.88 | 0.27 | | | | |
| 24 | 215 879.72 | 0.03 | 306 344.19 | 0.14 | | | 306 127.23 | 0.23 |
| 25 | | | 306 452.54 | 0.13 | 212 704.61 | -0.02 | 306 236.95 | 0.03 |
| 26 | 209 679.75 | -0.03 | 306 475.20 | 0.24 | 209 595.62 | -0.09 | | |
| 27 | 206 538.63 | 0.01 | 306 411.23 | 0.22 | | — | 306 199.16 | -0.11 |
| 28 | | | | | | | 306 050.15 | -0.18 |
| | | | 306 020.52* | -0.36 | | | | |
| | | $3 \rightarrow 2$ band | ¹ H ³⁵ Cl | | | $3 \rightarrow 2$ band | ¹ H ³⁷ Cl | |
| J | P (<i>J</i>) | Δ | R (<i>J</i>) | Δ | P(J)* | Δ | R(J)* | Δ |
| | | | 0/0 50/ 10 | 0.01 | | | 2(0,(02,05 | 0.00 |
| 0 | | | 209 /86.19 | -0.01 | | | 209 003.95 | -0.00 |
| 1 | 265 912.39 | -0.35 | 2/1631.70 | -0.06 | 205 / 35.91 | -0.23 | 2/1440.83 | -0.10 |
| 2 | 203 880.99 | -0.31 | 2/3414./4 | -0.19 | 203 /13./1 | 0.01 | 213 221.04 | -0.07 |
| 3 | 261 804.30 | -0.09 | 275 134.30 | -0.15 | 201 033.74 | -0.17 | 274 944.90 | -0.90 |
| 4 | 259 005.11 | -0.15 | 270 /89.20 | -0.05 | 259 497.92 | -0.10 | 210 397.43 | -0.20 |
| 2 | 25/4/1.04 | -0.13 | | | 257 507.18 | -0.12 | | |
| 07 | 152 022 02 | 0.24 | 201 252 27 | 0.26 | 255 002.70 | -0.35 | — | |
| é | 252 523.02 | -0.24 | 201 333.27 | -0.20 | 252 700.22 | -0.25 | 282 528 75 | |
| 0 | 230 371.91 | -0.09 | 282 737.09 | -0.09 | 230 418.73 | -0.19 | 282 938.73 | -0.34 |
| 10 | 245 701 25 | 0.08 | 285 204 02 | 0.01 | 245 575 85 | -0.14 | 285 002 76 | 0.03 |
| 11 | 243 721.23 | _0.00 | 286 463 63 | -0.13 | 243 083 10 | 0.12 | 205 092.70 | 0.02 |
| 12 | 240 681 81 | 0.14 | 287 550 07 | -0.02 | 240 544 40 | -0.0 4 | 287 357 07 | 0.14 |
| 13 | 238 004 37 | 0.07 | 288 581 67 | 0.02 | 240 344.40 | | 288 377 04 | 0.14 |
| 14 | 235 463 46 | -0.01 | 289 527 62 | -0.03 | 235 334 46 | -031 | 289 373 40 | -0.01 |
| 15 | 232 790 67 | -0.04 | | | 232 666 27 | -0.01 | 290 192 55 | -0.20 |
| 16 | | | 291 189 01 | -0.21 | 229 956 86 | -0.21 | 290 984 46 | -0.19 |
| 17 | 227 323 84 | -0.03 | 291 902.60 | -0.19 | 227 208 34 | -0.04 | 291 698.05 | -0.26 |
| 18 | 224 532.19 | -0.20 | 292 536.87 | -0.13 | 224 421.28 | -0.21 | 292 332.60 | -0.20 |
| 19 | 221 703.75 | -0.12 | 293 090.71 | -0.24 | | | 292 887.07 | -0.15 |

TABLE 5.—(cont.)

| | | | Тав | le 5.— | (cont.) | | | |
|----------------------|--|------------------------------|--|--------------------------|--|---------------------------|--|------------------------------|
| | | $3 \rightarrow 2$ band | ¹ H ³⁵ Cl | | | $3 \rightarrow 2$ band | ¹ H ³⁷ Cl | |
| J | $\mathbf{P}(J)$ | Δ | R(J) | Δ | P(<i>J</i>)* | Δ | R(J)* | Δ |
| 20 21 22 | 215 940.55 213 008.11 | -0.05 -0.15 | 293 563.75 293 954.55 — | -0.01 -0.02 | 218 737.97 215 843.87 212 916.29 | -0.03 0.03 -0.05 | 293 752.29 294 061.32 | -0.11 -0.12 |
| 23 24 25 26 | 210 043.71 207 047.80 | 0.03 -0.24 | 294 626.68 294 681.02 294 649.54 | 0.11 0.00 0.20 | 209 956.57 206 965.75 | -0.09 -0.20 | 294 287.43 — | 0.44 — |
| 27 28 29 | | | 294 029.50 | | | | | |
| - | | $4 \rightarrow 3$ band | ¹ H ³⁵ Cl | | | $4 \rightarrow 3$ band | ¹ H ³⁷ Cl | |
| J | P (<i>J</i>) | Δ | R(<i>J</i>) | Δ | P(J)* | Δ | R(J)* | Δ |
| 0 1 2 | | | 259 452.16 261 238.07 262 961 98 | -0.18 -0.28 -0.21 | 255 537.01 | -0.33 -0.58 | 259 285.54 261 069.14 262 790 94 | -0.22 -0.18 |
| 34 | 251 710.36 249 631.99 | -0.36 -0.08 | 264 622.32 266 218.17 | -0.33 -0.41 | 251 554.85 249 479.52 | -0.45 -0.24 | 266 042.81 | -0.25 |
| 5 6 7 | 247 498.44 245 311.39 243 072.14 | -0.16 -0.18 -0.10 | 267 748.65 269 212.18 270 607.52 | -0.15 0.03 0.01 | 247 349.43 245 165.76 242 929.86 | -0.09 -0.12 | 267 571.32 269 032.95 270 426.94 | -0.09 -0.11 0.06 |
| 8 9 10 | 240 781.72 238 441.54 | $-0.16 \\ -0.20 \\$ | 273 189.70 274 374.37 | -0.10 -0.17 | 240 642.97 235 921.55 | -0.21 | 273 006.44 274 140.17 | -0.13 -0.09 |
| 11 12 13 | 231 135.15 228 608.39 | -0.13 -0.25 | 275 486.90 276 525.88 277 490.21 | $0.00 \\ 0.05 \\ -0.08$ | 233 489.67 231 011.76 228 489.40 | $-0.13 \\ -0.12 \\ 0.10$ | 275 302.16 276 339.81 277 303.98 | $-0.41 \\ -0.18 \\ 0.05$ |
| 14 15 16 | 226 038.60 223 426.11 220 772.75 | $0.08 \\ -0.03 \\ 0.01$ | 279 191.67 | -0.04 | 225 923.24 223 315.30 220 666.39 | $-0.08 \\ 0.12 \\ 0.30$ | 279 004.80 | -0.06 |
| 17 18 19 20 | 218 079.80 215 347.97 212 578.63 209 773 12 | 0.26 0.23 0.10 0.04 | 280 583.32 281 656.50* | -0.27 | 215 250.27 212 485.50 | 0.34 0.24 | 280 396.90 280 973.97 281 470.47 281 887 16 | 0.34 0.04 0.77 0.16 |
| 21 22 23 | 206 932.49 | -0.06 | 282 404.81 282 654.48 282 820.70* | -0.19 -0.27 0.34 | | | 282 221.00 | -0.32 |
| | | $5 \rightarrow 4$ band | ¹ H ³⁵ Cl | | | $5 \rightarrow 4$ band | ¹ H ³⁷ Cl | |
| J | P (<i>J</i>) | Δ | R (<i>J</i>) | Δ | P (J)* | Δ | R(J)* | Δ |
| 0 | _ | | 250 859 01 | -0.12 | | | 250 704 12 | _0.70 |
| 23 | 241 629.31 | 0.06 | 250 858.01 252 522.11 254 122.67* | -0.12 -0.18 -0.45 | 243 449.00 241 489.03 | 0.05 0.05 | 250 704.15 252 368.92 253 965.96 | -2.01 0.25 |
| 4 5 6 | 239 610.11 | -0.24 | 255 659.23 257 129.95 258 533.95 | $-0.20 \\ -0.12 \\ 0.08$ | | - | 256 969.43 258 371.21 | 0.36 -0.09 |
| 7 8 | 233 229.48 230 998.62 | -0.02 0.01 | 261 136.61 | 0.21 | 233 102.02 230 874.07 | -0.33 | 260 971.14 | -0.04 |

| $5 \rightarrow 4 \qquad 5 \rightarrow 4 \\ \text{band} {}^{1}\text{H}^{35}\text{Cl} \qquad \qquad 5 \rightarrow 4 \ 5 \rightarrow 4 \$ | | |
|---|---|---------------|
| | H ³⁷ Cl | |
| J P(J) Δ R(J) Δ P(J)* Δ 1 | R (<i>J</i>)* | Δ |
| 9 228 717.79 -0.02 262 333.08 0.22 228 597.50 0.36 262 | 2 166.95 | 0.38 |
| 10 226 388.49 0.16 263 458.04 0.06 226 271.40 0.08 263 | 3 291.00 | 0.21 |
| 11 - 264 510.79 0.15 - 264 | 4 342.19 | -0.53 |
| 12 265 489.60 -0.16 265 | 5 321.22 | -0.07 |
| 13 266 394.22 -0.05 | | |
| 14 216 608.22 0.10 267 | 7 054.20 | 0.14 |
| 15 214 053.54 0.01 267 974.84* -0.32 | | |
| 16 268 649.43 0.01 | | |
| | | |
| 17 — 269 245.37 0.52 — — | _ | _ |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | | |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | ¹ H ³⁷ Cl R(<i>J</i>)* | Δ |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | — H ³⁷ Cl R(J)* | Δ |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | | Δ |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | | Δ |
| $ \begin{array}{cccccccccccccccccccccccccccccccccccc$ | | Δ |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | | Δ |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | | Δ |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | | Δ |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | | Δ |
| $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | | Δ |

TABLE 5.--(cont.)

^a Lines marked with an asterisk were excluded from the least-squares fits. The residuals are defined as $\Delta = \nu_{obs} - \nu_{calc}$, where ν_{calc} were produced from the parameters in table 3.

| TABLE 6.—VACUUM WAVENUMBERS ¹⁴ AND RESIDUALS (BOTH m ⁻¹) FOR THE $v \leftarrow$ | · 0 |
|--|-----|
| PROGRESSION ^a OF HCl | |

| | | 4 ← 0 band | ¹ H ³⁵ Cl | | | 4 ← 0 band | ¹ H ³⁷ Cl | |
|----|-----------------------|---------------|---------------------------------|-------|-----------------------|---------------|---------------------------------|-------|
| J | P (<i>J</i>) | Δ | $\mathbf{R}(J)$ | Δ | P (<i>J</i>) | Δ | R (<i>J</i>) | Δ |
| 0 | | | | | | | 1093 378.1* | 1.46 |
| 1 | 1090 194.1* | 0.68 | 1094 129.7* | 1.46 | 1089 448.0 | 0.45 | 1094 980.3 | 0.77 |
| 2 | 1087 867.0* | 0.98 | 1095 733.7 | 0.53 | 1087 124.8 | 0.98 | 1096 339.4 | -0.36 |
| 3 | 1085 300.6 | 0.23 | 1097 095.0 | 0.10 | 1084 562.5 | 0.12 | 1097 456.3 | 0.07 |
| 4 | 1082 497.4 | -0.43 | 1098 212.2 | -0.10 | 1081 764.2 | -0.39 | 1098 327.8 | -0.09 |
| 5 | 1079 459.5 | -0.33 | 1099 084.1 | -0.24 | 1078 731.5 | -0.36 | 1098 953.6 | -0.15 |
| 6 | 1076 187.7 | -0.13 | 1099 710.0 | -0.02 | 1075 465.7 | 0.04 | 1099 333.1 | 0.22 |
| 7 | 1072 684.0* | 0.66 | 1100 088.3 | -0.10 | 1071 968.6 | 1.11 | 1099 463.8 | -0.59 |
| 8 | | | 1100 218.0 | -0.61 | | | 1099 348.0 | 0.53 |
| 9 | | | 1100 099.7 | -0.10 | | | 1098 981.4 | 0.06 |
| 10 | _ | | 1099 731.0 | -0.22 | | _ | 1098 365.5 | 0.22 |
| 11 | _ | | 1099 111.6 | -0.54 | | | | |

| | ······ | | | | , | | | |
|--|---|--|--|--|--|-------------------------------|---|--|
| | | 5 ← 0 band | ¹ H ³⁵ Cl | | | 5 ← 0 band | ¹ H ³⁷ Cl | |
| J | $\mathbf{P}(\boldsymbol{J})$ | Δ | $\mathbf{R}(J)$ | Δ | P (<i>J</i>) | Δ | $\mathbf{R}(J)$ | Δ |
| 0 1 2 3 4 | 1337 538.9 1335 152.1 1332 465.9 1329 483.3 | 0.90 1.24 0.17 -0.71 | 1341 414.8* 1342 899.0 1344 081.1 1344 959.5 1345 532.9 | $ 1.72 \\ 0.46 \\ 0.02 \\ -0.10 \\ -0.19 $ | 1336 644.6 1334 261.5 1331 580.1 1328 602.4 | 0.91 1.14 0.38 -0.74 | 1340 515.0 1341 997.1 1343 178.3 1344 056.3 1344 630.1 | $ \begin{array}{r} 1.83 \\ 0.23 \\ -0.02 \\ -0.14 \\ -0.13 \end{array} $ |
| 5 6 7 8 9 | 1326 207.5 1322 637.6 1318 775.8 | 0.38 1.03 1.89 | 1345 798.9* 1345 762.6 1345 414.1 1344 758.8 1343 793.7 | -1.69 1.39 -0.01 0.29 -0.01 | 1325 332.3 1321 768.7 | 0.22 0.70 | 1344 897.1* 1344 862.0 1344 516.4 1343 864.3 | -1.63 0.96 0.06 0.45 |
| | | 6 ← 0 band | ¹ H ³⁵ Cl | | | 6 ← 0 band | ¹ H ³⁷ Cl | |
| J | $\mathbf{P}(\boldsymbol{J})$ | Δ | R (<i>J</i>) | Δ | P (<i>J</i>) | Δ | $\mathbf{R}(J)$ | Δ |
| 0 1 2 3 4 5 6 7 8 9 10 | 1574 598.4* 1572 151.1* 1569 344.7 1566 182.6 1562 666.6 1558 798.0* 1554 573.8 | 2.08 1.84 0.41 -0.22 0.31 1.78 -0.37 | $\begin{array}{c} 1578\ 413.4^*\\ 1579\ 777.0\\ 1580\ 779.5\\ 1581\ 418.4\\ 1581\ 689.1^*\\ 1581\ 601.6\\ 1581\ 142.0\\ 1580\ 315.6\\ 1579\ 121.5\\ 1577\ 557.7\\ 1575\ 624.0\\ \end{array}$ | $\begin{array}{c} 1.92 \\ -1.00 \\ -0.39 \\ -0.37 \\ -3.63 \\ 0.75 \\ -0.24 \\ -0.50 \\ -0.17 \\ -0.56 \\ -1.24 \end{array}$ | 1573 570.8 1571 128.1 1568 327.0 1565 169.9 1561 660.7 1557 799.9 — — | | 1577 381.0 1578 743.0 1579 744.1 1580 383.8 1580 655.7* 1580 569.7 1580 112.8 1579 290.1 1578 100.5 1576 542.4 | $\begin{array}{c} 1.96\\ -0.17\\ -1.18\\ -0.52\\ -3.57\\ 0.49\\ -0.45\\ -0.51\\ -0.01\\ 0.11\end{array}$ |
| - | | 7 ← 0 band | ¹ H ³⁵ Cl | | | $7 \leftarrow 0$ band | ¹ H ³⁷ Cl | |
| J | P (<i>J</i>) | Δ | R (<i>J</i>) | Δ | P (<i>J</i>) | Δ | R (<i>J</i>) | Δ |
| 0 1 2 3 4 5 6 7 8 9 | 1801 301.2 1798 793.9 1795 866.5 1792 522.7 1788 766.7 1784 500.0* | 2.17 2.26 0.49 -0.85 1.00 -93.97 | 1805 056.1 1806 298.8 1807 120.2 1807 517.1 1807 494.9* 1807 034.7 1806 154.3 1804 844 6 1803 107.2 1800 941.1 | $\begin{array}{r} 2.24 \\ -0.02 \\ -0.42 \\ -1.07 \\ 4.41 \\ -1.92 \\ -1.39 \\ -2.29 \\ -2.24 \\ -1.55 \end{array}$ | 1800 158.8 1797 653.3 1794 730.5 1791 394.1 1787 645.4 | | 1803 909.6 1805 148.7 1805 969.5 1806 366.2 1806 344.4 1805 889.6 1805 012.1 1803 705.9 1801 978.1 | 4.59 -0.06 -0.80 -2.37 1.83 -1.76 -1.97 -3.98 0.07 |

TABLE 6.—(cont.)

^{*a*} See footnote to table 5.

 0.29 m^{-1} , between the measured wavenumbers¹⁹ and those calculated according to the parameters in table 3. Because only one $(1 \rightarrow 0)$ band of ¹H³⁷Cl included in table 5 overlaps other input data, these bands provide a further test of the consistency of our results, over a large range of energy, in fact up to *ca*. 0.5 of the dissociation limit. Again the agreement is satisfactory.

In this work we have achieved one of the first determinations directly from experimental data (wavenumbers and frequencies of several isotopically related

molecules) of a mass-independent potential energy as a function of internuclear separation, either numerically by the R.K.R. procedure or analytically according to the Dunham form of equation. Some mass-independent properties⁴¹ characteristic of the $X \, {}^{1}\Sigma^{+}$ electronic state of HCl are its equilibrium internuclear separation

 $R_e = 1.274\ 6084 \times 10^{-10} \pm 1.5 \times 10^{-16} \,\mathrm{m}$

and the Hooke's-law coefficient

$$k_{\rm e} = 516.332 \ 15 \pm 6.4 \times 10^{-4} \ {\rm N \ m^{-2}}$$

derived from U_{01} and U_{10} , respectively. The outstanding coefficient a_0 in the Dunham potential-energy function is

$$a_0 = 4.194\ 235 \times 10^{-18} \pm 1.1 \times 10^{-23} \text{ J}$$

$$a_0 = 2.111393 \times 10^8 \pm 56 \text{ m}^{-1}$$

derived from $a_0 = U_{10}^2/(4U_{01})$ with or without a factor of *hc*, respectively. The mass-dependent expansion parameter γ , used in expressions for wavefunctions and matrix elements,⁴² is

$$\gamma \equiv 2U_{01}/(U_{10}\mu^{1/2}) = 7.082\,9816 \times 10^{-3} \pm 1.7 \times 10^{-8}$$

for ¹H³⁵Cl. The standard errors of the potential-energy coefficients a_i , $1 \le i \le 8$, are given in table 3, but the accuracy of the R.K.R. points is more difficult to assess. The relative accuracy of the points for v < 4 is probably ca. 10^{-6} ; although the difference $(R_{\max} - R_{\min})$ maintains this accuracy for states of v > 4, the absolute accuracy of each value of R_{\min} or R_{\max} may relatively decrease to ca. 10^{-3} . All these accuracies apply with respect to the Born-Oppenheimer approximation; adiabatic or non-adiabatic corrections^{43,44} may be significant.

CONCLUSIONS

In our analysis of a large collection of experimental frequencies and wavenumbers of some isotopic molecules of HCl we have reduced these data to a set of mass-independent parameters by means of weighted least-squares procedures with rigorous treatment of statistical significance. We have found that the combination of seven elemental mass coefficients $\Delta_{kl}^{\rm H,Cl}$, and either the equilibrium internuclear separation R_e and nine potential-energy coefficients $a_i, 0 \le i \le 8$, or 24 explicit energy coefficients in mass-reduced form U_{kl} suffices to reproduce satisfactorily not only the 896 fitted frequencies and wavenumbers but also other data of ³HCl and ¹H³⁷Cl not included in the fitting procedure. Furthermore essentially all the U_{kl} parameters determined in this fitting procedure are consistent with the potentialenergy function defined by these coefficients a_i . Therefore our potential-energy function has a good measure of physical reality within the range of energy up to 0.52 of the dissociation limit in the ground electronic state $X^{1}\Sigma^{+}$ of HCl.

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