SPECTROSCOPIC PARAMETERS AND POTENTIAL FUNCTION OF HCl MOLECULE

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Experimentally measured wavenumbers of rovibrational transitions of $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, $D^{37}Cl$ *molecules were used to find the parameters* $U_{mj}(m + j \le 4)$, Δ^{H}_{mj} *and* Δ^{Cl}_{mj} *of* HCl *molecule invariant for any isotopic modification. Correlations between* U_{mj} *parameters were taken into account when estimating them. The isotopic–invariant parameters of potential in the Dunham and Simons–Parr–Finlan representations were calculated in terms of independent spectroscopic parameters* U_{m0} *and* U_{m1}.

1. INTRODUCTION

The Hamiltonian, describing the rotational–vibrational motion of a diatomic molecule in a $^1\Sigma$ electronic state, may be presented in the form[1]

$$H = \frac{1}{2} P_r \frac{1}{\mu_{\text{vib}}} P_r + \frac{1}{2} \frac{\hbar}{\mu_{\text{rot}}\, r^2} \mathbf{J}^2 + V_0 + V_1, \qquad (1)$$

where r is internuclear distance, $P_r = -i\hbar \frac{\partial}{\partial r}$; $\mathbf{J}$ is the total angular momentum of a molecule, V_0 is the isotopic–invariant Born–Oppenheimer potential, V_1 is the nuclear–mass–dependent correction to the potential for the interaction between electronic states. When taking into account this interaction, the terms μ_{vib} and μ_{rot} include the corrections dependent on r and nuclear mass in addition to the reduced molecular mass.

Solution of the problem with the use of Hamiltonian (1), and the rigid rotator and harmonic oscillator being the initial approximation, yields the well–known expression for rovibrational energy levels

$$E_{vJ} = \sum_{m,\, j} Y_{mj} \left(v + \frac{1}{2} \right)^m [J\,(J+1)]^j, \qquad (2)$$

where v and J are the vibrational and rotational quantum numbers, Y_{mj} are the Dunham spectroscopic parameters. In this case, within the Dunham representation, the potential is a series over the parameter $z_{\text{D}} = (r - r_{\text{e}})/r_{\text{e}}$

$$V = a_0^{\text{D}} z_{\text{D}}^2 \left(1 + \sum_{n=1}^{\infty} a_n^{\text{D}} z_{\text{D}}^n \right), \qquad (3)$$

where r_{e} is the equilibrium internuclear distance.

The parameters Y_{mj}, as a function of nuclear masses, are presented by the following relationship[1]:

$$Y_{mj} = \mu^{-(2m+j)/2}\, U_{mj} \left[1 + \frac{m_{\text{e}}}{M_A} \Delta^{A}_{mj} + \frac{m_{\text{e}}}{M_B} \Delta^{B}_{mj} + 0\left(\frac{m_{\text{e}}^2}{M_i^2} \right) \right], \qquad (4)$$

where M_A and M_B are the masses of A and B atoms; $\mu = M_A M_B/(M_A + M_B)$ is the reduced mass of the molecule; m_{e} is the electron mass; U_{mj}, Δ^{A}_{mj}, and Δ^{B}_{mj} are the isotopic–invariant parameters.

Fitting of Eqs. (2) and (4) by the least squares method to the observed wavenumbers of different isotopic modifications of a molecule under study gives a set of parameters U_{mj}, Δ^{A}_{mj}, and Δ^{B}_{mj}. The latter, in its turn, bears information about the potential of the molecule and its kinetic characteristics.

Although the isotopic–invariant parameters U_{mj} are interrelated, the sets of independent parameters can be separated from them. Some expressions relating U_{mj} parameters are presented in Ref. 1, and more comprehensive information can be found in Refs. 2 and 3. In the present work the isotopic–invariant parameters U_{mj}, Δ^{H}_{mj}, and Δ^{Cl}_{mj} for HCl molecule were obtained from rovibrational wavenumbers taking into account the correlation between U_{mj} parameters. As far as we know the correlation between U_{mj} was not taken into account fully or partially (e.g., in Refs. 4 and 5 only the simplest relations for the low–order parameters were considered), when solving the inverse problems.

The coefficients a_i in the expansion for the Born–Oppenheimer potential V_0 correlate with the parameters U^*_{mj} what allows the potential parameters a_i to be expressed in terms of independent U^*_{mj} by simple algebraic relations. References 2 and 3 give the expressions for the parameters a_i in terms of U^*_{mj} for the potential expanded into the Dunham and Simons–Parr–Finlan series. The latter is the expansion of the potential over the parameter $z_{\text{s}} = (r - r_{\text{e}})/r$:

$$V = a_0^{\text{s}} z_{\text{s}}^2 \left(1 + a_1^{\text{s}} z_{\text{s}} + a_2^{\text{s}} z_{\text{s}}^2 + \ldots \right). \qquad (5)$$

The potential with the Simons–Parr–Finlan parameters gives, for large r, closer asymptote to the real potential as compared to the Dunham representation.

Using the relations $a_i^{\text{D}}(U^*_{mj})$ and $a_i^{\text{s}}(U^*_{mj})$ we determined the parameters of isotopic–invariant Born–Oppenheimer potential for the HCl molecule.

2. CALCULATIONS

We used two sets of experimental data for four isotopic modifications of HCl molecule, $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, and $D^{37}Cl$. The first set comprises 317 experimental wavenumbers from Refs. 6 and 7, its characteristics are

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presented in Table I. The second set includes the same data for $D^{35}Cl$ and $D^{37}Cl$ molecules and additionally the data for vibrational bands 0–0, 2–1, 1–1, and 3–2 for $H^{35}Cl$ and $H^{37}Cl$ molecules from Refs. 8 and 9. In addition, instead of the data for 1–0 band from Ref. 7, corresponding new data from Refs. 8 and 9 were used. Altogether 504 wavenumbers were involved in the second set.

Table I. Characteristics of the set I of observed wavenumbers[6,7] *used in the fitting.*

Band	J_{max}, $H^{35}Cl$		J_{max}, $H^{37}Cl$	
	R–branch	*P*–branch	*R*–branch	*P*–branch
1 – 0	31	30	22	19
2 – 0	12	12	11	11
3 – 0	11	9	9	8
	J_{max}, $D^{35}Cl$		J_{max}, $D^{37}Cl$	
2 – 0	21	15	15	14
3 – 0	16	16	14	15

Table II. Spectroscopic parameters U_{mj}, *in* cm^{-1} $(amu)^{m/2+j}$, *obtained from the fitting of two sets of experimental data*.*

	U_{mj} (I)	U_{mj} (II)
U_{10}	2960.1064(96)	2960.168(36)
U_{01}	10.37783(19)	10.3773(19)
U_{20}	– 51.5065(61)	– 51.559(37)
U_{11}	– 0.297489(36)	– 0.29758(16)
U_{30}	0.1316(19)	0.148(13)
U_{21}	$0.1496(27)\cdot 10^{-2}$	$0.157(10)\cdot 10^{-2}$
U_{40}	$-0.110(22)\cdot 10^{-2}$	$-0.28(16)\cdot 10^{-2}$
U_{31}	$-0.770(51)\cdot 10^{-4}$	$-0.92(17)\cdot 10^{-4}$
D^{H}_{10}	$-0.5322(58)\cdot 10^{-1}$	$-0.494(17)\cdot 10^{-1}$
D^{Cl}_{10}	0.12(14)	$0.52(60)\cdot 10^{-1}$
D^{H}_{01}	0.83(18)	$0.95(41)\cdot 10^{-1}$
D^{Cl}_{01}	– 8.2(13)	– 0.5(12)
U_{02}	$-0.510238(28)\cdot 10^{-3}$	$-0.51013(29)\cdot 10^{-3}$
U_{12}	$0.7088(13)\cdot 10^{-5}$	$0.7046(68)\cdot 10^{-5}$
U_{03}	$0.159869(50)\cdot 10^{-7}$	$0.15967(33)\cdot 10^{-7}$
U_{22}	$-0.414(13)\cdot 10^{-6}$	$-0.396(58)\cdot 10^{-6}$
U_{13}	$-0.514(13)\cdot 10^{-9}$	$-0.473(48)\cdot 10^{-9}$
U_{04}	$-0.7729(10)\cdot 10^{-12}$	$-0.7739(56)\cdot 10^{-12}$

* The experimental uncertainties are given in parentheses in terms of last digits indicated.

Both sets of experimental data were processed that yielded the values of independent isotopic–invariant parameters U_{m0}, U_{m1} and coefficients Δ^{H}_{10}, Δ^{Cl}_{10}, Δ^{H}_{01}, and Δ^{Cl}_{01}, which are tabulated in Table II. (Numbers I and II correspond to the number of a set). The experimental error in *i*th wavenumber was taken to be $\nu^{obs}_{i}\cdot 10^{-6}$. The parameters U_{02}, U_{12}, U_{03}, U_{22}, U_{13}, U_{04} expressed in terms of U_{m0} and U_{m1} were used in the fitting, so the parameters to be determined entered into the fitted equations nonlinearly. The inter–related parameters $U_{mj}(2 \le m + j \le 4)$ were calculated using the independent U_{m0} and U_{m1}. Their values are also tabulated at the bottom of Table II.

The isotopic–invariant parameters of potential were calculated in the Dunham and Simons–Parr–Finlan representations using the obtained values of independent parameters U_{m0} and U_{m1}. They are presented in Table III. For each representation we calculated two sets of potential parameters from two sets of experimental data and from two corresponding sets of parameters U_{m0} and U_{m1}.

Table III. Isotopic–invariant parameters of potential in the Dunham and Simins–Parr–Finlan representations obtained by fitting of two sets of experimental data.*

Parameter cm^{-1}	a^{D}_{i}(I)	a^{D}_{i}(II)	a^{s}_{i}(I)	a^{s}_{i}(II)
a_0	211080.5(41)	211100(39)	211080.5(41)	211100(39)
a_1	– 2.36273(17)	– 2.36330(89)	– 0.36273(17)	– 0.36330(89)
a_2	3.6694(11)	3.6692(54)	– 0.41882(63)	– 0.4207(33)
a_3	– 4.8121(84)	– 4.786(34)	– 0.3111(72)	– 0.289(27)
a_4	5.398(62)	5.30(24)	– 0.597(26)	– 0.58(11)
a_5	– 4.10(32)	– 4.2(13)	0.050(96)	– 0.23(35)
a_6	– 0.7(15)	1.1(60)	1.35(33)	1.6(13)

* Standard deviations of the least–squares fits are given in parentheses in terms of last digits indicated.

3. DISCUSSION

The rms discrepancy

$$\sqrt{\sum_{i} (\nu^{obs}_{i} - \nu^{calc}_{i})^2 / (M - N)}$$

(M is the number of experimental values, N is the number of fitted parameters, ν^{obs}_{i} is an observed wavenumber, ν^{calc}_{i} is its calculated value) was $0.552\cdot 10^{-2}$ cm^{-1} for the fit I and $0.809\cdot 10^{-2}$ cm^{-1} for the fit II. It is natural, since the experimental wavenumbers for HCl and DCl molecules were obtained by different authors, and superposition of systematic errors may take place in this case. Despite of that fact, the results of the fit II are, in our opinion, more realistic, since the corresponding set of experimental data contains more wavenumbers, some of them being new and more precise.

The obtained values for parameters Δ^{Cl}_{10} and Δ^{Cl}_{01} are statistically insignificant. It may be due to the uncertainty in determination of Δ_{mj} and as a result some of them must be fixed when performing the fitting.

Table IV presents the correlation matrix for spectroscopic parameters resulting from the fit II. Strong correlation between vibrational parameters U_{m0} should be noted that is due to the form of the Dunham potential. Large uncertainty in the higher–order parameters, a_5 and a_6, can be explained by the same reason. The obtained values of a^{s}_{5} and a^{D}_{6} are statistically insignificant.

Table IV. Correlation matrix for spectroscopic parameters obtained from the fit II.

	U_{10}	U_{01}	U_{20}	U_{11}	U_{30}	U_{21}	U_{40}	U_{31}	D_{10}^{H}	D_{10}^{Cl}	D_{01}^{H}	D_{01}^{Cl}
U_{10}	1.00	0.13	– 0.99	– 0.27	0.97	0.25	– 0.95	– 0.29	0.62	0.42	– 0.11	– 0.11
U_{01}		1.00	– 0.16	0.39	0.18	– 0.36	– 0.20	0.34	0.14	0.03	– 0.07	– 0.99
U_{20}			1.00	0.20	– 0.99	– 0.18	0.98	0.22	– 0.63	– 0.47	0.06	0.15
U_{11}				1.00	– 0.13	– 0.99	0.07	0.97	– 0.02	– 0.08	0.10	– 0.43
U_{30}					1.00	0.11	– 1.00	– 0.16	0.61	0.46	– 0.06	– 0.17
U_{21}						1.00	– 0.05	– 0.99	0.00	0.09	– 0.07	0.40
U_{40}							1.00	0.09	– 0.60	– 0.45	0.06	0.19
U_{31}								1.00	– 0.03	– 0.13	0.03	– 0.37
D_{10}^{H}									1.00	0.29	– 0.05	– 0.14
D_{10}^{Cl}										1.00	0.64	– 0.08
D_{01}^{H}											1.00	– 0.03
D_{01}^{Cl}												1.00

Unfortunately, the experimental data on hot bands of $H^{35}Cl$ and $H^{37}Cl$ from Refs. 10 and 11 were not included in the fitting. This is because the calculation of isotopic–invariant parameters needs for simultaneous use of experimental data on at least three isotopic modifications of a molecule in fitting. But experimental data on hot bands of DCl molecule analogous to those from Refs. 10 and 11 are inavailable. Their use in the fit would allow us to obtain more comprehensive data on the potential of HCl molecule.

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