

Dipole function for the C–H oscillator

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MS received 10 October 1995

Abstract. Using local mode description for methyl chloride, the infrared intensities for the first four CH₃ stretching overtone bands are used to calculate the dipole function for the C–H bond. Detailed expressions for overtone transitions for diatomic molecules derived by Bouanich are employed for the calculation of dipole moment derivatives.

Keywords. Dipole function; oscillator; local mode; overtone; methyl chloride.

1. Introduction

Normal modes of vibrations, with their corresponding normal coordinates, are satisfactory in describing the excitation to low lying vibrational levels which can be investigated by traditional infrared absorption or Raman spectroscopy. The normal mode description, however, become less satisfactory for explaining excitations to higher vibrational quantum states and dissociation processes involving vibrations with displacement of more than one symmetrically equivalent terminal atom (Hollas 1987). The actual process of the formation of a single atom of hydrogen on dissociation of benzene cannot be explained by the normal mode which envisages the energy being taken by the six hydrogen atoms in the normal mode of vibration. Local modes describe the high overtone levels and therefore the dissociation of the C–H bonds of benzene and other molecules with equivalent X–H bonds satisfactorily.

Though the concept of the local modes was introduced much earlier (Coblentz 1908; Ellis 1929; Mecke 1932, 1933, 1936, 1950), it was sort of rediscovered and developed after 1968 (Martin and Kalanter 1968; Wallace 1976; Mckean 1978; Sage 1978; Quack 1981; Watson *et al* 1981; Menefee *et al* 1982; Child and Halonen 1984; Amrein *et al* 1984; Child 1985; Henry 1987).

It is found that the intensity of the C–H vibrational overtone is determined by additive equal contributions of all local C–H bond modes of the XH_n groups (Burberry *et al* 1979; Burberry and Albrecht 1979a). The intensity of 0 → 6 overtone of benzene is roughly six times as large as the intensity of the C–H oscillator in C₆D₅H (Swofford *et al* 1977). Intensities of overtone bands in terms of local modes can be explained by using two different approximations of the dipole functions: (i) exponential bond dipole form, and (ii) series expansion in the internal displacement coordinates (Schek *et al* 1979; Sage 1984; Findsen *et al* 1986; Lewerenz and Quack 1986; Tarr and Zerbetto 1989; Kjaergaard *et al* 1990, 1991).

Albrecht and co-workers (Burberry *et al* 1979; Burberry and Albrecht 1979a) have reported intensities of C–H stretching local mode overtones for a variety of

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hydrocarbons. It was found that, for a given overtone, all C–H local modes contribute equally to the intensity. The intensity per C–H bond was found to be remarkably constant. This has also been highlighted by Sage and Jortner (1981) in a review on ‘bond modes’. Thus, overtone intensities for the C–H bond can be computed from the overtone intensities of hydrocarbons with several equivalent C–H bonds. Assuming these C–H bond overtone intensities are representative of the intensities of the diatomic C–H oscillator, Burberry and Albrecht (1979b) employed the intensities for the C–H bonds in benzene for the evaluation of its first and second dipole moment derivatives using a simple quadratic dipole function. It is, in general, realized that the local mode states are only weakly coupled and the dipole moment consists of the superposition of separate contributions for each bond dipole term (Sage and Jortner 1981).

The dipole functions for diatomic molecules were determined using IR intensity data as well as molecular orbital calculations. Singh and Luck (1981) have surveyed various expressions for transition moment matrix elements for vibrational transitions in the infrared spectra of diatomic molecules reported by various authors. In a series of articles by Bouanich and others, complete expressions for the vibrational matrix elements for diatomic molecules have been given (Bouanich 1974, 1976, 1987; Bouanich and Brodbeck 1975, 1976; Bouanich and Ogilvie 1986). The expressions were obtained following the approach of the perturbed harmonic oscillator and include (Bouanich 1974, 1976; Bouanich and Brodbeck 1975, 1976) among others the fourth, fifth and sixth order contributions to the dipole moment function. With the available data on the overtone intensities of the C–H local mode of CH₃X molecules (Ahmed and Henry 1987), we use the expressions for transition moment matrix elements for the diatomic oscillator with higher orders as reported by Bouanich and Brodbeck (1975, 1976) and evaluate the comprehensive dipole function for the C–H bond.

2. Mode of calculation

Assuming Dunham’s (1932) internuclear potential

$$V(\xi) = hca_0\xi^2(1 + a_1\xi + a_2\xi^2 + \dots) \quad (1)$$

where ξ is the reduced displacement from the equilibrium internuclear separation. $\xi = (r - r_e)/r_e$ and a_0, a_1, a_2, \dots have their usual meaning, Bouanich (1974, 1976) assumed the vibrational perturbation in terms of the normal coordinate, q

$$H'_{\text{vib}} = hc\omega_e(bq^3 + dq^4 + gq^5 + lq^6 + mq^7 + nq^8), \quad (2)$$

and derived the expressions for transition moments, $\mathbf{R}_v^{v'}$ as follows

$$\mathbf{R}_v^{v'} = \sum_i M_i \alpha^{(-i/2)} \mathbf{R}_i^{v-v'} \quad (3)$$

where v and v' designate the initial and final quantum numbers, M_i designate the various dipole moment derivatives and $R_i^{v-v'}$ are coefficients of the i^{th} dipole moment derivative for $v \rightarrow v'$ transitions. The normal coordinate, q is defined as $q = \alpha^{(1/2)}(r - r_e)$, where $\alpha = \omega_e/2B_e r_e^2$, ω_e is harmonic frequency and B_e is the rotational constant. The expressions for the constants used in the above equations are summarized below

(Bouanich 1974, 1976; Tipping and Ogilvie 1976), $a = (\omega_e x_e / B_e)^{1/2}$; $\omega_e x_e$ is anharmonicity constant $a_0 = D_e a^2$; where dissociation energy $D_e = D_0^0 + \frac{1}{2}\omega_e$

$$a_i = 2^{i+2} - 2 \times a^i (-1)^i / (i+2)! \quad (4)$$

$$b = \frac{a_1 \gamma^{1/2}}{2}; d = \frac{a_2 \gamma}{2}; g = \frac{a_3 \gamma^{3/2}}{2}; l = \frac{a_4 \gamma^2}{2}; m = \frac{a_5 \gamma^{5/2}}{2}; n = \frac{a_6 \gamma^3}{2} \text{ and } \gamma = \frac{2B_e}{\omega_e}$$

and the expressions for $R_i^{v-v'}$ are given by Bouanich (1974, 1976).

3. Results and discussion

Infrared intensities for the first four overtones for methyl chloride, reported by Ahmed and Henry (1987), are used for present calculations. The values are similar for all methyl halides reported. The oscillator strengths are reduced to absolute intensities and transition moment matrix elements using the following expression:

$$f = 1.8771 \times 10^{-12} A \cdot (\text{cm mol}^{-1}), \quad (5)$$

where f is the integrated oscillator strength and A the integrated absorption coefficient, and

$$A_{v'}^{v} = \frac{8\pi^3 N v^{v'}}{3hc} \times |\mathbf{R}_{v'}^{v}|^2, \quad (6)$$

where N is the Avogadro number, v is the frequency in cm^{-1} , h is Planck's constant, \mathbf{R} is the transition moment, c is the velocity of light in cm s^{-1} and $A_{v'}^{v}$ is the integrated absorption coefficient for $v \rightarrow v'$ transition in cm mol^{-1} . Absolute intensities and transition moments are given in table 1. The values of constants like ω_e , $\omega_e x_e$, B_e , r_e etc. employed in these calculations are given in table 2. The ω_e , $\omega_e x_e$, and r_e values correspond to the C–H bond for CH_3Cl whereas the rotational constant and the dissociation constant values for the C–H bond are taken from the data collected by Herzberg (1950) for the C–H radical since these values for the C–H bond of CH_3Cl are not available. Burberry and Albrecht (1979b) as well as Sage and Jortner (1981) and Schek *et al* (1979) have compared the dipole function results for the C–H bond with those of the C–H radical. It is found that (Sage and Jortner 1981) exponential dipole

Table 1. Absolute intensities* (A_0^i), transition moment elements[#] (\mathbf{R}_0^i) and symmetry weighed frequencies** (v_0^i) for the first four overtones of methyl chloride.

i	A_0^i (cm mol^{-1})	\mathbf{R}_0^i (Debye)	v_0^i (cm^{-1})
2	4.2598×10^4	5.3560×10^{-3}	5896.3
3	6.0172×10^3	1.6571×10^{-3}	8647.0
4	6.1573×10^2	4.6384×10^{-4}	11265.0
5	5.3628×10^1	1.2373×10^{-4}	13777.0

* CH_3 intensities for methyl chloride derived from oscillator strengths given by Ahmed and Henry (1987) were divided by 3 to obtain the values for intensities for C–H oscillator; [#] For signs of R_0^i see text; ^{**} Symmetry weighted frequencies as reported by Ahmed and Henry (1987)

Table 2. Molecular parameters for methyl chloride used for the calculation.

ω_e^a (cm ⁻¹)	$\omega_e X_e^a$ (cm ⁻¹)	B_e^b (cm ⁻¹)	r_e^c (Å)	D_0^{0b} (eV)
3007.3	62.5	14.457	1.0860	3.47

^aValues derived for CH₃ group of methyl chloride from infrared data; ^bValues for C-H radical taken from the literature (Herzberg 1950); ^cValue for r_e taken from Duncan (1970)

Table 3. Values of a , a_i and α used for the calculation with $i = 0$ to 6 for methyl chloride

a	a_1	a_2	a_3	a_4	a_5	a_6	α
2.0792	-2.0792	2.5218	-2.2472	1.6094	-0.9715	0.5090	88.1879

Table 4. Values of $\alpha^{-i/2} R_i^{0 \rightarrow n}$ for C-H oscillator in methyl chloride for $i = 1$ to 4 and $n = 0, 2$ to 5.

n	i			
	1	2	3	4
0	1.6532×10^{-2}	6.1252×10^{-3}	3.6028×10^{-4}	1.1821×10^{-4}
2	-7.9160×10^{-3}	7.6449×10^{-3}	7.9668×10^{-4}	3.5337×10^{-4}
3	1.3592×10^{-3}	-4.0304×10^{-3}	8.2078×10^{-4}	1.2123×10^{-4}
4	-3.0501×10^{-4}	5.4859×10^{-4}	-4.0025×10^{-4}	8.2043×10^{-5}
5	8.2360×10^{-5}	-1.6918×10^{-4}	1.6123×10^{-4}	-7.1003×10^{-5}

function with $R^*/R_{eq} = 0.75$ (R^* marks the maximum of dipole function) can be used to reproduce the theoretical dipole function of the C-H radical in the ground state for $0.4 < R/R_{eq} < 1.15$ which is in good agreement with the value of this parameter found from the analysis of the intensity data for C-H bond modes. In the absence of appropriate data available for the C-H oscillator, molecular constants like B_e and D_0^0 for the C-H radical have been taken as close approximations for the present calculations. The values of a_i obtained by using the above constants in (4) are given in table 3.

The values of the coefficient $R_i^{0 \rightarrow n}$ where $i = 1$ to 5 and $n = 0$ to 5 as obtained by using expressions of Bouanich (Bouanich and Brodbeck 1975, 1976) are given in table 4. The expressions used for $R_i^{0 \rightarrow n}$ with $i = 1$ to 5 and $n = 0$ to 5 are derived from general expressions for $R_i^{v \rightarrow v+n}$ reported by Bouanich and are given in the appendix. The signs of the transition moment matrix elements given in table 1 are indeterminate. For calculations on the CO molecule Bouanich (1974, 1976) and others assumed that the transition moments alternate in sign from R_0^0 onwards, assuming that the permanent dipole moment R_0^0 for CO bond is negative. In the present calculations, however, all possible sign combinations of R_0^2 , R_0^3 , R_0^4 and R_0^5 are considered for the calculations of M_i values. By solution of four simultaneous equations for R_0^2 , R_0^3 , R_0^4 and R_0^5 , the values of M_1 , M_2 , M_3 and M_4 have been calculated using the expressions for R_0^v (3). The M_0

Table 5. Dipole moment derivatives and the derived parameters for the C-H oscillator in methyl chloride. Units of M_i are $\text{D}(\text{\AA})^{-i}$.

Symbols*	M_0	M_1	M_2	M_3	M_4	R^* (Å)	μ_{\max} (D)
+ - + -	1.475	-0.842	-0.053	-0.762	-0.837	0.151	2.198
- - + +	1.481	-0.809	-0.799	-3.362	-8.410	0.736	1.684
- + + -	1.488	-1.076	-1.413	-2.776	-2.443	0.421	1.918
- - + -	1.449	0.591	0.189	-1.767	-2.035	1.391	1.579
+ + + -	1.512	-2.509	-1.655	-1.771	-1.245	0.151	2.908
- + + +	1.518	-2.476	-2.402	-4.371	-8.818	0.656	2.185
+ - + +	1.505	-2.242	-1.042	-2.357	-7.212	0.631	2.224
+ + + +	1.543	-3.909	-2.644	-3.366	-7.620	0.586	2.780

*Symbols correspond to the signs of R_i^i for $i = 2$ to 5.

values are calculated employing the following expression (Bouanich 1974, 1976) using $R_0^0 = 1.46$ D (Moody and Thomas 1971),

$$M_0 = R_0^0 - \sum_{i=1} M_i \alpha^{(-i/2)} R_i^{0 \rightarrow 0}, \quad (7)$$

where $\alpha^{(-i/2)} R_i^{0 \rightarrow 0}$ is the coefficient of dipole moment derivative. The values of dipole moment versus Δr were calculated for all these combinations using the expression $M(\Delta r) = \sum_i M_i (\Delta r)^i$. The dipole functions of those sign combinations which lead to a minimum instead of a maximum were discarded. The values of M_i for $i = 0$ to 4, the values of internuclear distances for maximum dipole moment R^* and the corresponding dipole moments μ_{\max} for these sign combinations are given in table 5.

In figure 1 are shown the plots of dipole functions obtained in terms of the Taylor expansion for a reduced number of sign combinations considered. Since the Taylor series expansions are more reliable in the vicinity of equilibrium distances, the quality of function depends on the limit of truncation. The functions are found to drop suddenly at internuclear distances away from the equilibrium distances and in many cases assume negative values. The Taylor series functions for C-H oscillator are found to be similar to those obtained for CO molecule as reported in earlier studies (Bouanich 1974, 1976; Figeys and Geerlings 1991; Jameson 1991).

4. Conclusions

Molecular electronic property surfaces as shown in (7) above are emerging into their rightful place next to potential energy surfaces (Jameson 1991). For example, dipole function reflects the basic features of the electronic distribution of the molecule. In the present studies the comprehensive dipole function for C-H oscillator has been evaluated using the detailed treatment of Bouanich (Bouanich 1974, 1976; Bouanich and Brodbeck 1975, 1976) and the experimental infrared intensities of the overtone bands for CH_3Cl considering local mode description of the CH_3 group. Since the Taylor series expansions are more reliable in the vicinity of equilibrium distances, the quality of function depends on the limit of truncation of the function. The functions are found to drop suddenly at internuclear distances away from the equilibrium distances and in many cases assume negative values. However, the Taylor series functions for C-H oscillator are found to be similar to those obtained for CO molecule as reported in

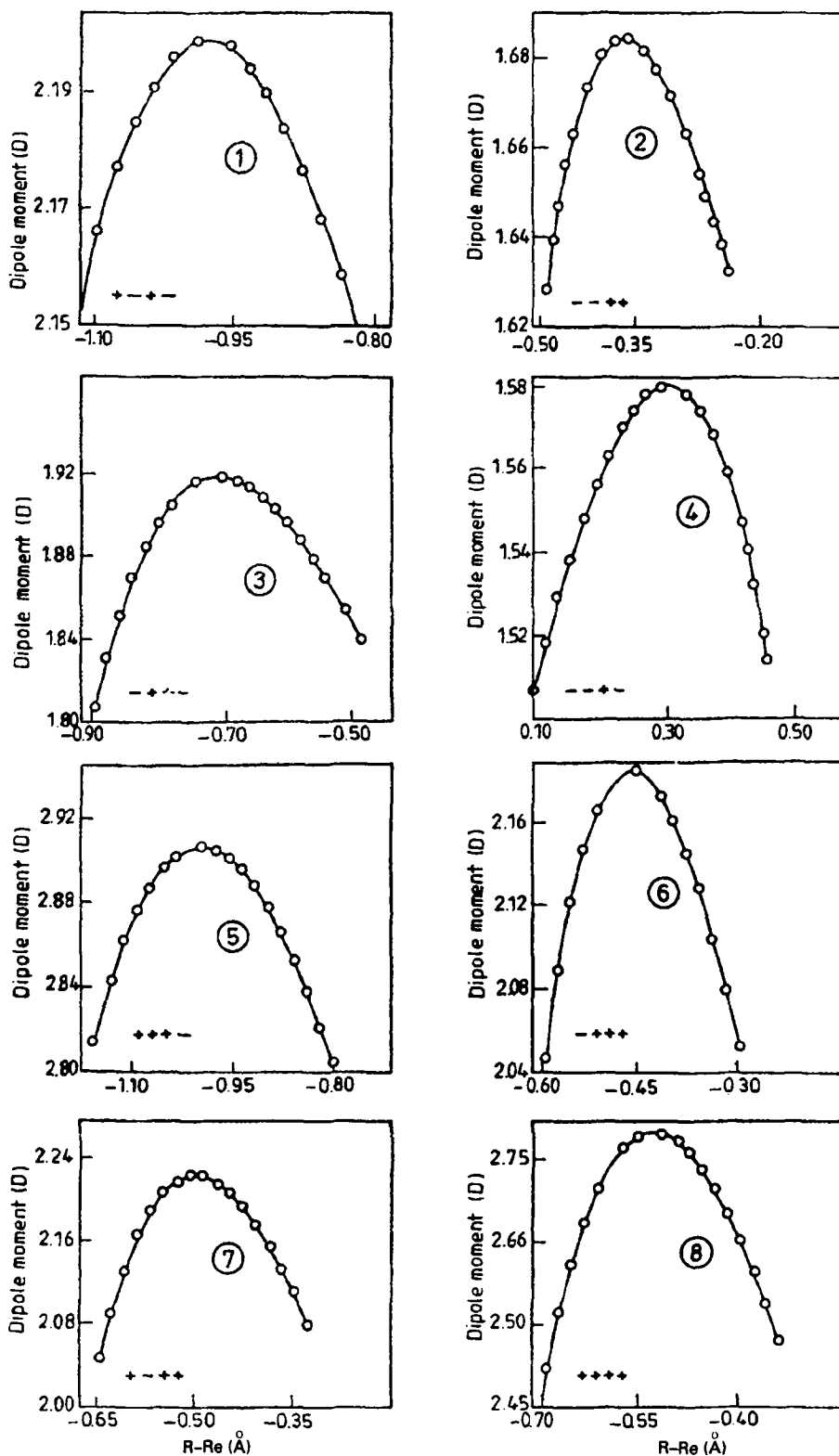


Figure 1. Plots of variation of dipole moment for C-H oscillator with internuclear distance for methyl chloride. The sign combinations shown for each plot correspond to the signs of transition moment integrals.

earlier studies (Bouanich 1974, 1976; Bouanich and Brodbeck 1975, 1976; Jameson 1991). The lack of knowledge of exact sign combination of transition moment integrals, however, remains a handicap for choosing the right dipole function and for the interpretation of the derived results. In the present calculations a bond dipole model is assumed to describe the molecular dipole function using local mode theory of the C–H bonds. The assumptions may be expected to break down in molecules like methyl cyanide in which there are π bonds.

Acknowledgements

One of us (AFJ) thanks the Indian Institute of Technology, Madras for a research fellowship.

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