A quantitative theory of infrared spectra

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A quantitative treatment of the frequencies and intensities of lines in infrared spectra of diatomic molecules is outlined, with particular reference to HCl. The relationship of classical and quantum-mechanical approaches to the analysis of such spectra and to ideas of molecular structure is discussed.

1. Introduction

Woolley (1976) has questioned the meaning of molecular structure within quantum mechanics, especially in relation to spectroscopic experiments on isolated molecules containing a few nuclei and their associated electrons. According to Woolley, if a description of a given experiment uses molecular eigenstates, then no structural interpretation is possible. The implicit assumption of microscopic rigidity, inherent in classical ideas about molecular structure but apparently inconsistent with a general quantum-mechanical theory of molecular eigenstates, arises as an asymptotic approximation in quantum mechanics, and emerges through the transition from quantum to classical chemistry. However, the idea of a molecular structure is a *useful approximation* in chemistry, although there exist molecules for which the idea of a fairly rigid arrangement in space corresponding to a definite, almost static geometrical array of nuclei and characterized by bond lengths and interbond angles, is misleading. Some instances of these exceptions are NH_3, PF_5, $Fe(CO)_5$, XeF_6 and $C_{10}H_{10}$ (bullvalene and isobullvalene). For *diatomic* molecules however, analogous problems are less severe (Woolley and Sutcliffe 1977), and we present a *quantitative* analysis of the infrared spectra of a diatomic molecule within the Born–Oppenheimer approximation.

The measurement of infrared spectra began about 1890. For the particular gaseous substance HCl Ångström and Palmaer (1893) detected the first absorption line, within the transparency range of the materials then available as windows on sample cells, to have a frequency $\sim 8\cdot7 \times 10^{13}$ Hz. Thousands of lines in such rotational or vibrational bands have now been measured from the millimetre-wave region to the green in the visible spectrum, for various isotopic combinations of ^1H, ^2H or ^3H with ^{35}Cl or ^{37}Cl. If the gaseous sample is sufficiently rare that intermolecular effects are negligible, then the principal features of each absorption line that one may attribute to molecular properties are the frequency at which absorption is a maximum and the integrated intensity. These two features must be accounted for within any satisfactory theoretical treatment of the observable phenomena. According to the quantum theory, the transition energies correspond to the energy separations of the molecular quantum states, and the transition intensities are related to matrix elements connecting the different states.

2. The quantitative theory

To derive the energies of the quantized molecular states, we first assume the Born–Oppenheimer separation of electronic and nuclear motions, and then attribute the observed transitions to be related to the vibrational and rotational motions of the nuclei in the field of the electrons. We have determined the vibrational energies E_v from the quantization condition according to the WKBJ method (Ogilvie and Tipping 1983):

$$\frac{\hbar}{B_e^{1/2}} \oint [E_v - V(x)]^{1/2}\,dx + \sum_{j=2} \left(\frac{\hbar}{i}\right)^j \oint y_j(x, E_v)\,dx = h(v + 1/2)$$

in which v is the vibrational quantum number, h is Planck's constant, x is a reduced interatomic separation, $x = (R - R_e)/R_e$, $V(x)$ is the interatomic Born–Oppenheimer potential energy, and the y_j are defined by a recurrence formula (Ogilvie and Tipping 1983). Noting the proportionality of the integrand in the first WKB integral to a component of linear momentum, p_x,

$$p_x \sim [E_v - V(x)]^{1/2}(2M)^{1/2}$$

we are reminded of the action integral

$$\oint p\,dr = nh$$

arising in the elaboration by Wilson and Sommerfeld of Bohr's theory of the one-electron atom. The sum of higher WKB integrals of y_j is obviously an asymptotic series in powers of the reduced Planck constant $\hbar$. For a potential-energy function $V(x)$, Dunham (1932) used the form

$$V(x) = a_0 x^2 \left(1 + \sum_{j=1} a_j x^j\right)$$

that clearly has a precursor in the work of Kratzer (1920). An alternative function (Ogilvie 1981)

$$V(z) = c_0 z^2 \left(1 + \sum_{j=1} c_j z^j\right)$$

in terms of the argument $z = 2(R - R_e)/(R + R_e)$ places the united-atom and separated-atom limits on an equivalent basis; consequently this series does not suffer from the restricted range of convergence of Dunham's. By means of *computer algebra* (Ogilvie 1982), the vibrational energies E_v may be found as analytic functions of the masses M_j of the separated atoms, the Hooke's law coefficient k_e, the equilibrium internuclear separation R_e, and the potential-energy coefficients a_j or c_j, $j > 0$. Following Dunham (1932), the rotational effects may formally included in terms of $\beta = J(J + 1)$, J being the quantum number for angular momentum, and B_e the equilibrium rotational parameter:

$$V(x), \beta)/B_e = \gamma^{-2} x^2 \left(1 + \sum_{j=1} a_j x^j\right) + \beta/(1 + x)^2$$

Here γ is the limiting ratio $2B_e/\omega_e$ of rotational and vibrational transition intervals, lying within the range $10^{-4} < \gamma < 2 \times 10^{-2}$ for known diatomic molecules. Thus the vibration-rotational energies E_{vJ} in terms of M_j, K_e, R_e and a_j or c_j have been found

explicitly up to a_{12} or c_{12} in the leading terms (resulting from the first WKB integral) and up to a_{10} or c_{10} in the correction terms. Although we have used the quasi-classical WKBJ procedure in order to produce these expressions, those obtained through Rayleigh–Schrödinger perturbation theory are exactly the same (Bouanich 1978). For the actual fitting of frequencies of vibration-rotational transitions, the form (Ross *et al.* 1974)

$$E_{vJ} = \sum_{k=0} \sum_{l=0} U_{kl}(k_e^{BO}, R_e^{BO}, a_j \text{ or } c_j)[\mu^{-1/2}(v+1/2)]^k$$

$$\times [\mu^{-1}J(J+1)]^l \left[1 + m_e\left(\frac{\Delta_{kl}^a}{M_a} + \frac{\Delta_{kl}^b}{M_b}\right) + \cdots \right]$$

is useful; the coefficients U_{kl} that result from only the first WKB integral have formally no mass dependence, but the reduced mass $\mu = M_a M_b/(M_a + M_b)$ does appear in the following two factors. The final factor takes account of various effects; specifically the coefficients $\Delta_{kl}^{a;b}$ of the ratio m_e/M_j of electronic and atomic masses include other WKB integrals, adiabatic and non-adiabatic effects resulting from the breakdown of the Born–Oppenheimer approximation, relativistic effects, etc. The parameters k_e^{BO} and R_e^{BO} take values with which predictions from (so-called) *ab initio* quantum computations should strictly be compared.

The intensities of vibration-rotational lines are proportional to the squares of the matrix elements, $|\langle vJ|M^e|vJ'\rangle|^2$, of the electric dipole-moment function M^e. Within the Born–Oppenheimer separation, we write the dipole-moment function as a power series:

$$M^e(x) = \sum_{j=0} M_j^e x^j$$

Then the matrix elements of the dipole moment may be reduced to sums of matrix elements of powers of x:

$$\langle vJ|M^e(x)|v'J'\rangle = \sum_{j=0} M_j^e \langle vJ|x^j|v'J'\rangle$$

The latter have been analytically derived from the energies E_{vJ} through vibrational and rotational wavefunctions as a convenient computational procedure, although these wavefunctions should be regarded as artefacts of the particular computational approach. Vibration–rotational interaction results in effects on line intensities that are expressed in the Herman–Wallis (1955) factor $F_v^{v'}$, a ratio essentially related to the intensity of a particular line and the intensity of the entire band. This factor may be written as a power series,

$$F_v^{v'}\left(\frac{\beta'-\beta}{2}\right) \equiv \frac{|\langle vJ|M^e(x)|v'J'\rangle|^2}{|\langle v,0|M^e(x)|v',0\rangle|^2} = 1 + C_v^{v'}\left(\frac{\beta'-\beta}{2}\right) + D_v^{v'}\left(\frac{\beta'-\beta}{2}\right)^2 + \cdots,$$

in which the coefficient $C_v^{v'}$ contains a linear dependence upon the coefficients M_j^e. By this means one can determine the signs of the electric dipole-moment matrix elements $\langle v|M^e|v'\rangle$ of which the band intensities are proportional to the square. The form of the dipole-moment function as a power series possesses the familiar defect of diverging outside the range of x in which it is defined from experimental data. An alternative representation as a Padé function,

$$M^e(x) = M_0^e(x+1)^3/\left(1 + \sum_{j=1}^{7} e_j x^j\right),$$

incorporates the behaviour appropriate at the limits of the united atom, $M(x) \propto R^3$ as $R \to 0$, and of the separate atoms, $M(x) \propto R^{-4}$ as $R \to \infty$, for HCl.

The values of parameters thus sufficing to define the frequencies (Coxon and Ogilvie 1982) and intensities (Ogilvie and Tipping 1985) of the vibration-rotational transitions of HCl in the range $0 \leq v \leq 7$ are given in the table as an instance of the successful application of the theory.

Potential-energy, dipole-moment and other molecular parameters of HCl.

j	c_j	$M_j^e/10^{-30}\,\text{C m}$	e_j
0	$(2\cdot111393 \times 10^7 \pm 56)\,\text{m}^{-1}$	$3\cdot64729 \pm 0\cdot0025$	
1	$-1\cdot3633725 \pm 3\cdot5 \times 10^{-5}$	$4\cdot02071 \pm 0\cdot130$	$1\cdot89762 \pm 0\cdot036$
2	$0\cdot865517 \pm 0\cdot00020$	$0\cdot1282 \pm 0\cdot193$	$0\cdot87296 \pm 0\cdot095$
3	$-0\cdot473118 \pm 0\cdot0014$	$-4\cdot9641 \pm 0\cdot327$	$1\cdot3321 \pm 0\cdot17$
4	$0\cdot08959 \pm 0\cdot0106$	$-3\cdot2949 \pm 0\cdot50$	$1\cdot9871 \pm 0\cdot30$
5	$0\cdot15645 \pm 0\cdot044$	$-2\cdot1598 \pm 0\cdot63$	$1\cdot2573 \pm 0\cdot49$
6	$-0\cdot6061 \pm 0\cdot17$	$-3\cdot1555 \pm 0\cdot77$	$3\cdot1344 \pm 0\cdot74$
7	$-0\cdot375 \pm 0\cdot69$	$0\cdot070 \pm 1\cdot7$	$2\cdot5470 \pm 1\cdot2$
8	$1\cdot26 \pm 2\cdot2$		

$R_e^{BO} = (1\cdot2746084 \times 10^{-10} \pm 3\cdot5 \times 10^{-16})\,\text{m}$ 　　　 $\Delta_{0,1}^H = 0\cdot1320 \pm 0\cdot0007$

$\Delta_{1,0}^H = -0\cdot06382 \pm 0\cdot00088$ 　　　　　　　　　　　　 $\Delta_{0,1}^{Cl} = -0\cdot250 \pm 0\cdot017$

$\Delta_{1,0}^{Cl} = 0\cdot1280 \pm 0\cdot016$ 　　　　　　　　　　　　　 $\Delta_{1,1}^H = 0\cdot462 \pm 0\cdot019$

$\Delta_{2,0}^H = -0\cdot3824 \pm 0\cdot017$ 　　　　　　　　　　　　 $\Delta_{0,2}^H = 0\cdot74 \pm 0\cdot04$

According to Primas (1981), molecular structure is a classical concept and should be represented by classical observables. It is useful to compare this quantum approach to a purely classical treatment. We note that the energy coefficients Y_{kl} in the term-value equation (Dunham 1932)

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

are sums of terms in powers of $\gamma = 2B_e/\omega_e$:

$$Y_{kl} = \gamma^n(\ldots a_j \ldots) + \gamma^{n+2}(\ldots a_{j+4} \ldots) + \ldots$$

of which the first term is proportional to U_{kl}. Analogously the vibrational matrix elements of x^j (Tipping and Ogilvie 1976):

$$\langle v|x^j|v'\rangle = \gamma^n(\ldots a_j \ldots) + \gamma^{n+1}(\ldots a_{j+2} \ldots) + \ldots$$

and the Herman–Wallis coefficients (Tipping and Ogilvie 1982):

$$C_v^{v'} = \gamma(\ldots a_j, M_j^e \ldots) + \gamma^2(\ldots a_j, M_j^e \ldots) + \ldots$$

are also written as series in powers of γ. Tipping (1972; cf, also Tipping and Ogilvie 1986) has shown that classical mechanics leads to expressions for these three quantities of which at least the leading terms are identical to those obtained according to the quantum-mechanical treatment. Thus although the numerical values of parameters listed for HCl in the table might vary slightly as a result of a classical treatment, the nature of the results remains qualitatively the same. Numerical trajectory calculations of the dipole matrix elements (Stine and Noid 1983) lead to similar agreement between the quasi-classical and quantum approaches.

Obviously the ideas of two masses oscillating about their mean positions as if attached through a spring, or rotating about their common centre of mass with a certain angular velocity, are classical in nature. In quantum mechanics, the spatial properties of eigenstates characterized by values of a set of quantum numbers $v, J, \ldots$ are independent of time; for these states, a distribution function of relative positions of nuclei, or electrons (Ezra and Berry 1982), or both electrons and nuclei (Thomas 1969), may be defined.

3. Conclusions

(1) Molecular structure is a classical concept, and care is required in its use in the rigorous quantum-mechanical treatment of eigenstates.

(2) Molecular structure can be introduced into, and imposed upon, quantum-mechanical treatments via the Born–Oppenheimer approximation.

(3) Molecular structure and vibrational and rotational spectroscopy can be adequately treated according to classical theory, or equivalently in some cases by quasi-classical or quantum-mechanical methods within the Born–Oppenheimer approximation.

(4) Algebraic methods, with the complicated computations done efficiently and accurately by machine, produce results with general applicability.

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