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Finite Electric Field Valence Shell Calculations of Polarizability Gradients and Raman Depolarization Ratios for Diatomic Molecules

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Calculation of polarizability gradients have been made for a number of diatomic molecules using the Finite Field CNDO/II approximate SCF method. Comparison with experimental results suggests that the method will be generally useful for the prediction and interpretation of Raman intensities.

Es wurden die Polarisierbarkeitsgradienten einer Anzahl zweiatomiger Moleküle mit Hilfe der CNDO/II–SCF Näherungsmethode mit endlichem Feld durchgeführt. Der Vergleich der Ergebnisse mit experimentellen Werten zeigt, daß diese Methode allgemein zur Vorhersage und zur Interpretation von Raman-Intensitäten geeignet ist.

Introduction

Measurement of the absolute intensities and depolarization ratios of vibrational Raman lines leads, in principle, to a determination of the derivative with respect to the appropriate normal co-ordinate of the mean value of the polarizability tensor. The following relation holds for unpolarized incident light:

$$I_p = A\,[45\,(\overline{\alpha}')^2 + 13\,(\gamma')^2]\ , \tag{1}$$

where I_p is the intensity of the scattered light and A is a factor depending on the temperature, the frequency and intensity of the incident light, the frequency of the Raman shift, the degeneracy of the normal mode and the molar concentration. The quantities $\overline{\alpha}'$ and γ' are respectively the mean value and anisotropy of the polarizability gradient. This relation, combined with the equation defining the depolarization ratio for unpolarized incident light ϱ_n:

$$\varrho_n = \frac{6\gamma'^2}{45\,(\overline{\alpha}')^2 + 7\gamma'^2} \tag{2}$$

then yields a value for $\overline{\alpha}'$. A fuller discussion of the experimental determination of polarizability derivatives is given in Ref. [1].

Experimental work on Raman intensities has been quite extensive [2, 3] but few theoretical calculations have been reported. The advent of the laser source has provided the stimulus for further experimental measurements of these quantities and it therefore seems appropriate to present here the results of our calculations of polarizability derivatives and to compare them with existing experimental values.

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Apart from the delta-function model used by Long and Plane [4] and a consideration of dispersion forces by Oksengorn [5], the only molecular calculations of polarizability derivatives appear to have been concerned with the simple diatomics H_2^+ and H_2 [6–10]. In this communication we present calculations of polarizability derivatives for the stretching vibration of some diatomic molecules using a valence-orbital semi-empirical SCF-MO method.

Method of Calculation

In calculating polarizabilities and their derivatives we have used the Finite-Field CNDO/2 method described elsewhere [11]. The polarizability of each molecule was calculated at intervals of 0.005 Å up to 0.01 Å either side of the calculated field-free equilibrium bond length R_e. The polarizability derivatives were then obtained as the slope, at R_e, of the variation in α with change in bond length R. The relation between α and R was found in all cases to be linear in the range of R values examined. By performing the calculations with the electric field along ($\|$) and perpendicular to ($\perp$) the bond axis, the derivative of the mean value of the electronic polarizability is then obtained as

$$\bar{\alpha}' = \frac{\partial \bar{\alpha}}{\partial R} = \frac{1}{3}\left(\frac{\partial \alpha_{\|}}{\partial R} + 2\frac{\partial \alpha_{\perp}}{\partial R}\right), \tag{3}$$

where the normal co-ordinate in this simple case is R.

For linear molecules the square of the anisotropy of the derived polarizability tensor reduces to

$$\gamma'^2 = (\alpha'_{\|} - \alpha'_{\perp})^2 \tag{4}$$

and the depolarization ratio for unpolarized light ϱ_n is then

$$\varrho_n = \frac{6\,(\alpha'_{\|} - \alpha'_{\perp})^2}{45\,(\bar{\alpha}')^2 + 7\,(\alpha'_{\|} - \alpha'_{\perp})^2}\,. \tag{5}$$

Table 1. H_2

	$\alpha'_{\|}$	$\alpha'_{\perp}$	$\bar{\alpha}'$	ϱ_n
This work	1.280	0.000	0.427	0.500
Bell and Long	1.86	1.31	1.49	0.018
Tang and Albrecht	2.351	1.009	1.456	0.100
	2.506	0.931	1.837	0.088
	5.537	2.762	1.909	0.212
Hirschfelder	1.02	0.89	0.93	0.012
	1.08	0.80	0.89	0.003
	1.02	0.98	0.99	0.003
	1.10	0.95	1.00	0.002
Ishiguro *et al.*	1.9695	1.1319	1.4111	0.045
Kolos and Wolniewicz	1.776	0.831	1.146	0.082
Expt.[a]	1.69	0.85	1.13	0.07
Expt.[b]	1.98	0.96	1.30	0.073

[a] Ref. [14].

[b] Ref. [15].

Table 2

	This work						Expt.[a]	This work	Expt.[b]
Molecule	Bond order	$\alpha'_Q(\|\|)$	$\alpha'_{sp}(\|\|)$	$\alpha'(\|\|)$	$\alpha'_\perp$	$\bar{\alpha}'$	$\bar{\alpha}'$	ϱ_n	ϱ_n
N_2	3.000	2.096	0.488	2.584	0.600	1.261	1.73	0.139	0.18
							1.75		0.19
O_2	2.000	2.540	0.702	3.242	0.055	1.117	1.48	0.479	0.33
							1.46		0.26
CO	2.770	0.610	1.190	1.800	1.164	1.376	1.44	0.0275	0.31
							1.50		0.29
F_2	1.000	1.256	0.161	1.417	−0.095	0.409	0.110[c]	0.583	0.110
HF	1.275	1.260	0.057	1.317	−0.427	0.756	–	0.388	–
O_2^-	1.500	4.058	1.247	5.305	0.545	2.132	–	0.374	≃0.06[d]

[a] Values from Refs. [19, 2] respectively unless otherwise stated.

[b] The value obtained in Ref. [2] is quoted followed by the literature value given in Ref. [2].

[c] Ref. [16].

[d] Ref. [18].

Our calculated values of $\alpha'_{||}$, $\alpha'_\perp$, $\bar{\alpha}'$ and ϱ_n are shown in Tables 1 and 2. We shall discuss the results obtained for the hydrogen molecule separately from those obtained for the remaining diatomic molecules.

The Hydrogen Molecule

In the Finite Field CNDO/2 approximation the solution of the problem of the hydrogen molecule in a static uniform electric field directed along the molecular axis may be obtained analytically. The expression for the parallel polarizability component so obtained is [11]

$$\alpha_{||} = \frac{R^2}{\gamma_{AA} - \gamma_{AB} - 2\beta}, \tag{6}$$

where R is the internuclear separation and $\beta = \beta^0_{AB} S_{AB}$ in the notation of Pople and Segal [12]. The electron repulsion integrals γ_{AA} and γ_{AB} are calculated as the two-centre Coulomb integrals involving valence orbitals using formulae given by Roothaan [13]. Thus, differentiating the expression for $\alpha_{||}$ with respect to R we have

$$\alpha'_{||} = 2\left(\frac{\alpha_{||}}{R}\right) - \left(\frac{\alpha_{||}}{R}\right)^2 \left[\frac{\partial \gamma_{AA}}{\partial R} - \frac{\partial \gamma_{AB}}{\partial R} - 2\beta^0_{AB}\frac{\partial S_{AB}}{\partial R}\right]. \tag{7}$$

Using the value of $\alpha_{||}$ given earlier [11] ($\alpha_{||} = 0.457 \text{Å}^3$ at $R = 0.741114 \text{Å}$) together with the original values of β^0_{AB} and the hydrogen 1*s* orbital exponent of Pople and Segal we obtain $A' = 1.2798 \text{Å}^2$ in agreement with the value found by calculating the polarizability near the equilibrium distance where the relation between $\alpha_{||}$ and R was found to be linear.

Since the method used here considers only 1*s* orbitals on the hydrogen atoms $\alpha_\perp$ is always zero and so, therefore, is $\alpha'_\perp$. Consequently our calculated value of $\bar{\alpha}'$ is just $\frac{1}{3}\alpha'_{\|} = 0.4266\,\text{Å}^2$ compared with the experimental figures $1.13\,\text{Å}^2$ and $1.30\,\text{Å}^2$ [14, 15]. Our value for $\alpha'_{\|}$ of $1.2798\,\text{Å}^2$ compares very well with both experiment and previous calculations; it is closer to the experimental value than any of the different values quoted by Tang and Albrecht [10] and Hirschfelder [6]. The restriction of the basis set to 1*s* orbitals is clearly quite a severe one as our low value for $\bar{\alpha}'$ indicates. This is not an inherent restriction in the method and the result obtained for $\alpha'_{\|}$ suggests that inclusion of higher orbitals may also yield a reasonable value for α'.

Diatomic Molecules

In Table 2 we present the results of calculations of $\bar{\alpha}'$ and ϱ_n for some First Row diatomic molecules.[1] Comparison of $\bar{\alpha}'$ and ϱ_n with experiment is possible only for N_2, O_2 and CO, while a value for ϱ_n for F_2 can be obtained from the value of ϱ_s (for polarized incident light) given in Ref. [16] from the relation [17]

$$\varrho_s = \frac{\varrho_n}{2 - \varrho_n}\,. \tag{8}$$

A value for ϱ_n has also been estimated for O_2^- [18]. The agreement between our calculated values of $\bar{\alpha}'$ and the experimental ones of both Yoshino and Bernstein [14] and Spiro and Fontal [19] is good. The agreement is best for CO for which we calculate $\bar{\alpha}' = 1.376\,\text{Å}^2$, compared with the experimental value of $1.44\,\text{Å}^2$ and $1.50\,\text{Å}^2$. The values of $\bar{\alpha}'$ for N_2 and O_2 are also in good agreement with experiment.

Our calculated values of the depolarization ratios ϱ_n for N_2 and O_2 are in good agreement with the experimental results of Yoshino and Bernstein and with the literature values quoted by these authors. For the CO molecule our value of 0.0275 is an order of magnitude smaller than the experimental results. This arises from the relatively large $\alpha'_\perp$ calculated for this molecule, implying that the field-induced mixing of 2*s* and 2*p* orbitals on the carbon and oxygen atoms is quite sensitive to variation in bond length.

An approximate value of 0.06 for the depolarization ratios of the Raman band of O_2^- in a host lattice has been obtained by Holzer *et al.* [18]; our value of 0.374 suggests that the calculated contribution of $\alpha_\perp$ is underestimated, provided that the experimental value can be assumed to be close to that for the free ion. For the F_2 molecule our value of ϱ_n is slightly higher than that deduced from the experimental measurements of Claasen, Selig and Shamir [16] but is of the correct order of magnitude.

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[1] Correlations between bond order and bond polarizability derivatives have frequently been suggested. Bond orders are also listed in Table 2, and it can be seen that for the neutral molecules studied here the very simple relationship

$$\bar{\alpha}' \simeq 0.5P\,\text{Å}^2$$

reproduces the calculated average polarizability gradients with an accuracy of about $\pm 0.2\,\text{Å}^2$.

The negatively charged O_2^- ion, which is calculated to have a much higher value of $\bar{\alpha}'$ than for any of the neutral molecules, does not conform to this trend.

It is interesting to note that for the fluorine containing molecules HF and F_2 we calculate a negative sign for $\alpha'_\perp$. In the CNDO/2 valence shell approximation, $\alpha_\perp$ arises purely from the one-centre mixing of $2s$ and $2p$ orbitals and in the case of HF from this effect on the fluorine atom alone. Therefore a negative sign for $\alpha'_\perp$ means that the field induced dipole moment due to $2s$ and $2p$ mixing decreases as the bond length increases.

In order to obtain more insight into the factors contributing to $\bar{\alpha}'$ we have calculated the charge displacement and $2s$–$2p$ hybridisation polarizability derivatives and these are listed in Table 2. They are defined in the following way. To first order in the electric field F, we can write

$$\mu_i^F = \mu_i^0 + \alpha_{ij} F_j \tag{9}$$

in conventional notation.

In the CNDO/2 method, the total dipole moment can be expressed as the sum of a charge displacement term and a term arising from $2s$–$2p$ mixing [11, 12]

$$\mu_i^F = \sum_{\mathrm{A}} (Z_{\mathrm{A}} - P_{\mathrm{AA}}^F)\, i_{\mathrm{A}} - \frac{5}{\sqrt{3}} \sum_{\mathrm{A}} \frac{1}{Z'_{\mathrm{A}}} P^{F\cdots}_{2s,2p_i(\mathrm{A})}\,, \tag{10}$$

where $i = x, y$ or z. Assuming that the bond density matrix is a differentiable function of the normal co-ordinate we have:

$$\frac{\partial}{\partial Q}(\mu_i^F) = \frac{\partial}{\partial Q}\left[\sum_{\mathrm{A}} (Z_{\mathrm{A}} - P_{\mathrm{AA}}^F)\, i_{\mathrm{A}}\right] - \frac{5}{\sqrt{3}} \sum_{\mathrm{A}} \frac{1}{Z'_{\mathrm{A}}} \frac{\partial}{\partial Q}(P^F_{2s,2p_i(\mathrm{A})}) \tag{11}$$

or, to first order in F,:

$$(\alpha)'_{ij} = (\alpha_Q)'_{ij} + (\alpha_{sp})'_{ij}\,. \tag{12}$$

Since $(\alpha_Q)'_{ij}$ is a function of the cartesian co-ordinates of the atoms it might be expected that this term will be the dominant one. For all the molecules studied, except CO, this is found to be the case. For CO the situation is reversed, α'_{sp} being approximately twice α'_Q for this molecule. The contribution of $2s - 2p$ mixing to the zero-field dipole moment of CO is roughly three times the charge displacement term and clearly for this molecule the hybridization term is the more sensitive to perturbation.

Conclusion

There is a generally good correlation between our calculated polarizability derivatives and the experimental values. The agreement for corresponding depolarization ratios is reasonable, bearing in mind the fact that these are proportional to the *square* of the calculated polarizability gradient anisotropies. For the series of molecules studied, the factors determining the Raman transition probabilities can thus be fairly well interpreted within a valence orbital scheme. Further work on diatomic and larger molecules is in progress.

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