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Original Investigations

Coupled Calculation of Vibrational Frequencies and Intensities

I. Calculation of Intensities by a CNDO/2 Method with Extended Basis Set

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The combination of normal coordinate analysis with intensity calculations gives quantitative information about molecular force fields and the assignments of vibrational frequencies. Calculations of vibrational intensities by means of a standard CNDO/2 version give rise to satisfactory results for the IR intensities. However, the calculated Raman intensities often differ strongly from the experimental data. Inclusion of $2p$-polarization functions on hydrogen in the usually used valence basis set is quite successful to obtain improved molecular polarizabilities as well as Raman intensities.

Key words: Vibrational frequencies and intensities – Intensities and vibrational frequencies.

1. Introduction

Since 1930 normal coordinate calculations have been developed, yielding the vibrational frequencies and the corresponding normal coordinates of any molecule [1]. The main problem in these calculations is the determination of a unique physically significant set of force constants. Such calculations take into account only one dimension of the spectra. The second dimension, the intensity, could be very useful to ascertain the assignment of the vibrations, to choose between some probable sets of force constants and to obtain further information about several properties of the vibrating molecule.

2. Method

The calculation of vibrational intensities requires the knowledge of the derivatives of the dipole moment μ and the polarizability α with respect to the normal coordinates Q. In principle for both, IR and Raman spectroscopy, the inclusion of

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electrical anharmonicity and for the Raman spectroscopy the frequency dependence of the polarizability, as well as vibronic interactions, have to be considered. For larger molecules such an approach would mean an impossible expenditure. For the sake of simplicity it is justified to neglect electrical anharmonicity and to presuppose the conditions of Placzek's polarizability theory [2] to be fulfilled. The best attempts to calculate the values $(\partial\mu/\partial Q)$ and $(\partial\alpha/\partial Q)$ employ quantum chemical methods.

In general *ab initio* calculations need much more computer capacity than the semi-empirical methods. Therefore it is reasonable to use the latter for all calculations concerning large organic molecules, even when the lower quality of the calculated properties has to be taken into account. A comparison of the semi-empirical methods shows [3] that the CNDO method [4] yields dipole moments in good agreement with the observed values, and so this method has been chosen to calculate vibrational intensities. It was first applied by Segal and Klein [5] for the calculation of IR and by Bleckmann [6] for Raman intensities.

The integrated IR intensity A_k of a normal mode k is given by:

$$A_k = \frac{8\pi^3 N_0 \tilde{\nu}_k}{3h} g_k b_k^2 \left(\frac{\partial\mu}{\partial Q_k}\right)_0^2, \qquad (1)$$

where g_k is the degeneracy of the corresponding normal mode k and b_k is the vibrational amplitude of that mode. This leads to results which are directly comparable with experimental intensities [1].

In the case of Raman spectra, for observation at right angle to the laser beam using linear polarized incident light, the absolute scattering cross section is defined as:

$$S_k = \frac{2^4\pi^4}{1 - \exp(-hc\tilde{\nu}_k/kT)} (\tilde{\nu}_0 - \tilde{\nu}_k)^4 g_k b_k^2 (\alpha_k'^2 + (7/45)\gamma_k'^2) \qquad (2)$$

α' and γ' are the mean value and the anisotropy of the derivative of the polarizability tensor, respectively.

The derivatives $\partial\mu/\partial Q$, $\partial\alpha/\partial Q$ and $\alpha = \partial\mu_{\text{ind}}/\partial E$ have been evaluated by numerical differentiation, where μ_{ind} is the dipole moment induced in the molecule by an external electric field E. The finite displacements of the nuclei were chosen equal to the zero point amplitude of the appropriate normal mode and are calculated using the $\boldsymbol{L}$ vectors of the preceding normal coordinate analysis [7]. It was supposed that a linear relationship holds between μ and Q as well as α and Q. All polarizability calculations described in this paper were performed using a static electric field with a field strength of $5.142 \cdot 10^4$ V/m (0.001 a.u.) which is of the order of magnitude of the field strengths of commercial continuous wave gas lasers.

The CNDO calculated dipole moments as well as IR intensities are quite satisfactory. All papers dealing with polarizabilities and Raman intensities show, however, that there are significant differences between calculated and experimental data (see, for example, Refs. [6] and [8]).

In order to calculate the polarizability the perturbation of a molecule by an electric field can be handled using the methods of second-order perturbation theory [9] or be included directly into the Hamiltonian of the used quantum chemical method [10, 11]. For the latter the Hartree–Fock matrix element within the framework of the CNDO/2 method for molecules containing first-row and second-row elements and for an electric field in σ-direction ($\sigma = x, y, z$) may be written as follows:

$$F_{\mu\mu} = -\tfrac{1}{2}(I_\mu + A_\mu) + ((P_{AA} - z_A) - \tfrac{1}{2}(P_{\mu\mu} - 1))\gamma_{AA} + \sum_{B \neq A} (P_{BB} - z_B)\gamma_{AB} - \sigma_A E_\sigma \tag{3a}$$

$$F_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}\gamma_{AB} - \langle \mu_A(2s)|\sigma|\nu_A(2p_\sigma)\rangle E_\sigma \tag{3b}$$

$\mu_A(2s)$ and $\nu_A(2p_\sigma)$ are the Slater functions of the corresponding orbitals on atom A. σ_A is the appropriate Cartesian coordinate of this atom. The other symbols have their usual meaning [4]. The differences between calculated and observed values for the polarizabilities are largely due to the fact that for the first-row elements the $F_{\mu\nu}$ term does not contribute to the calculated polarizability.

For the hydrogen molecule itself, the perpendicular polarizability is calculated to be zero, whereas the experimental value is about 70% of the parallel polarizability. This disadvantage due to the restriction to valence orbital basis sets in the CNDO procedure can be removed by including polarization functions into the calculation.

In 1975 Shinoda *et al.* [12] and recently Nørby-Svendsen *et al.* [13] reported polarizability calculations using different orbital basis sets or polarization functions, respectively. They found that extension of the basis sets together with an adjustment of parameters used in the calculations improves the results for the calculated polarizabilities.

In order to calculate Raman intensities of the fundamental vibrations of larger molecules in reasonable computer time, we restricted our calculations to the addition of 2*p*-polarization functions on hydrogen atoms which are, together with carbon, the most important atoms in organic compounds.

In 1969 Davies [10] showed that similar calculations on HF resulted in an equilization of charge on both atoms. A reasonable charge distribution was obtained by a modification of the bonding parameter β^0_{AB}.

To find the best value for the orbital exponent $\xi_{2p}(H)$ of the included extra orbitals on hydrogen and the modified bonding parameter β^0_{AB}, we calculated the polarizability values for the hydrogen molecule as well as for the water molecule and the electron densities of the hydrogen atoms in the water molecule for the following combinations:

a) $\beta^0_{AB} = \tfrac{1}{2}\chi(\beta^0_A + \beta^0_B)$ with $\chi = 1/N$ ($N = 1, 2, 3, \ldots 8$) ($N = 1$ in the standard CNDO/2 version)
b) $\xi_{2p}(H) = 2.0 - 0.8$ with $\Delta\xi = 0.4$ for each value of the bonding parameter.

The results are shown in Figs. 1 and 2. Like Davies [10] we found that for $\chi = 1$ a large donation of electrons to the hydrogen atoms takes place (see Fig. 2). The best values of χ and $\xi_{2p}(H)$ for polarizability calculations seem to be 1/4 and about 1, respectively.

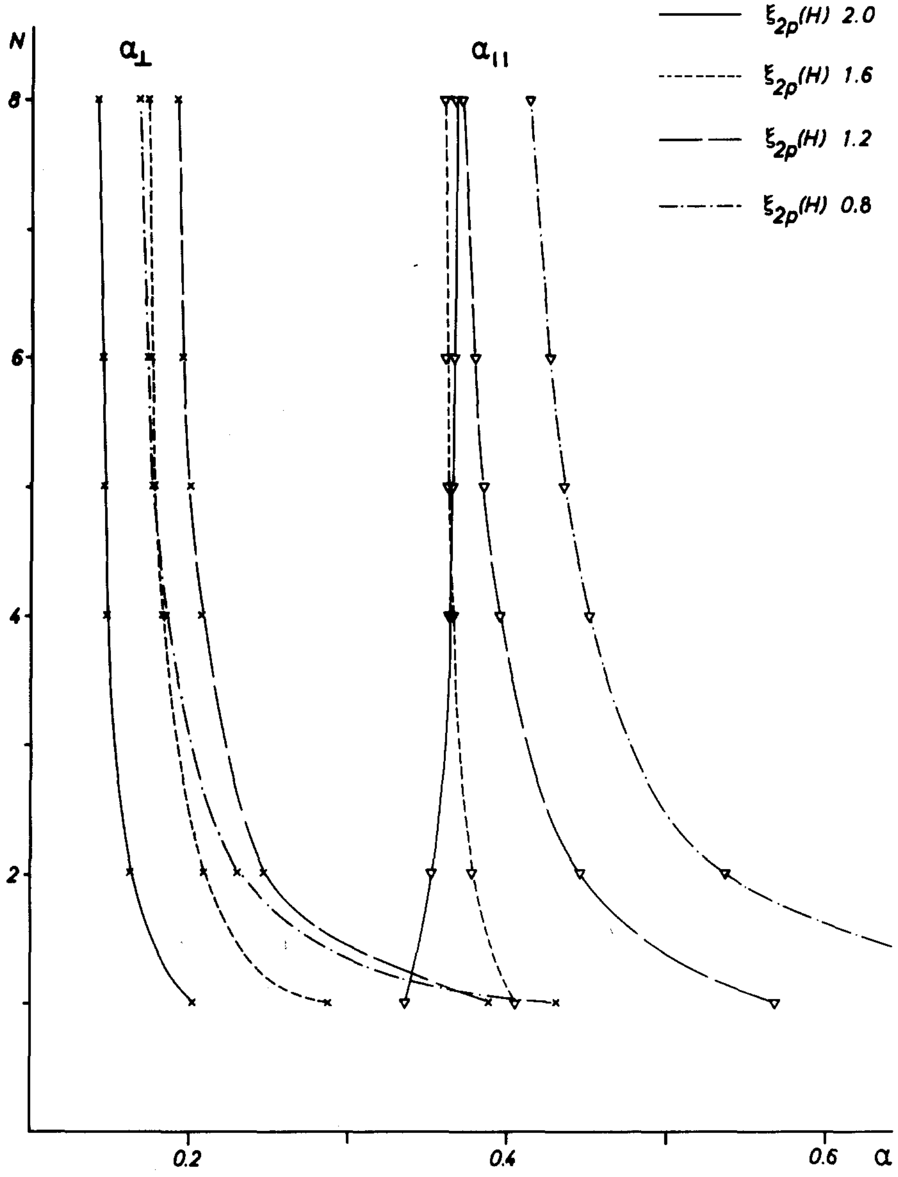

Fig. 1. Polarizabilities $\alpha_{\|}$ and $\alpha_{\perp}$ (10^{-24} cm^3) of hydrogen for different combinations of the orbital exponent ξ_{2p}(H) and the bonding parameter (see text)

The calculated dipole moments for an orbital exponent of $\xi_{2p}(\mathrm{H}) = 1.0$ are very different from the experimental values (see for comparison Fig. 4).

Since the calculation of intensities requires much computer time (see Fig. 3) one has to look for a compromise in the value of the orbital exponent ξ_{2p}(H) in order to get satisfactory results for IR and Raman intensities with only *one* calculation.

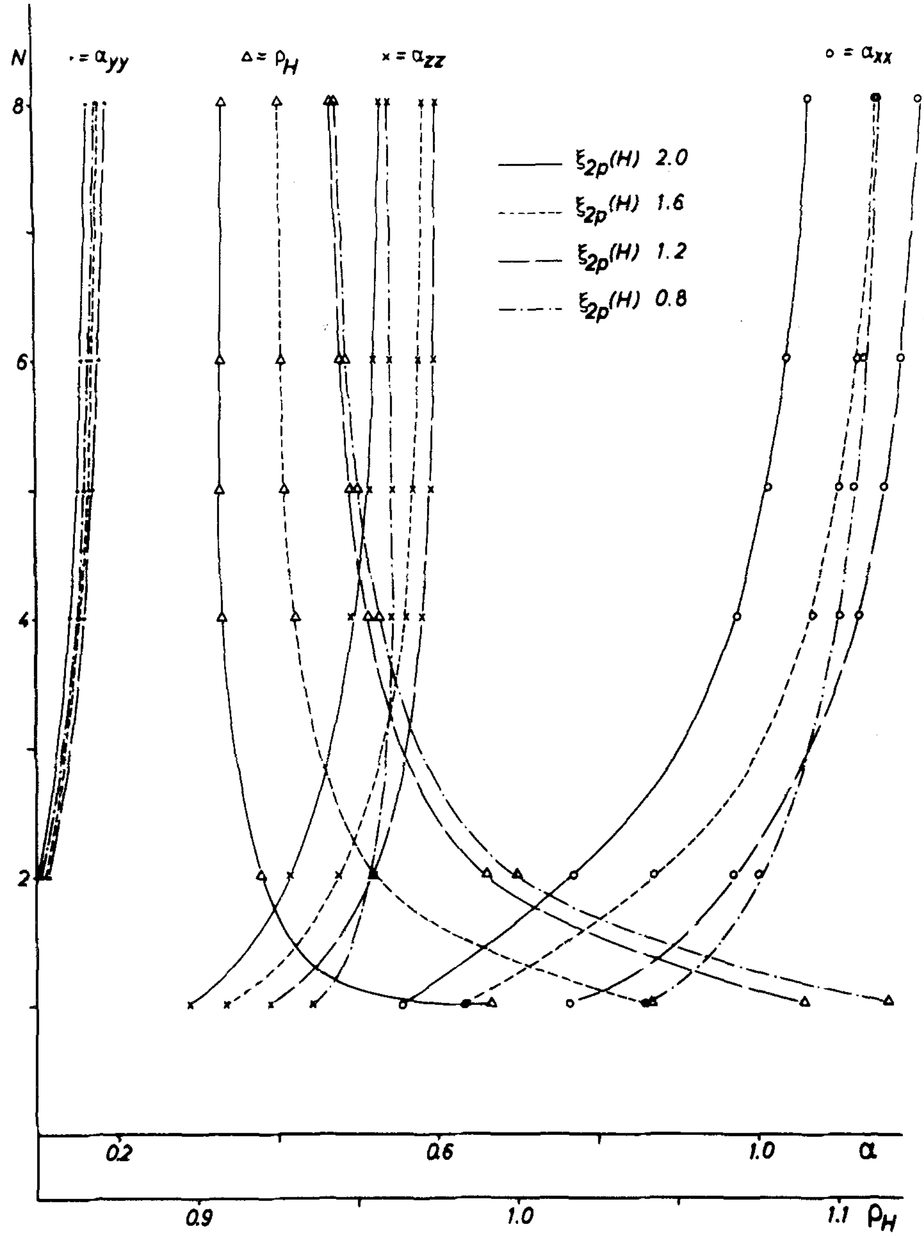

Fig. 2. Polarizabilities α (10^{-24} cm^3) and electron densities on hydrogen atoms ρ_H for the water molecule calculated with different combinations of the orbital exponent $\xi_{2p}(H)$ and the bonding parameter (see text)

Thus we plotted

$$\Delta\mu\% = \frac{\mu_{\text{exp}} - \mu_{\text{calc}}}{\mu_{\text{exp}}} \cdot 100$$

for the water molecule and

$$\Delta\alpha\% = \frac{(\alpha_{\perp}/\alpha_{\parallel})_{\text{exp}} - (\alpha_{\perp}/\alpha_{\parallel})_{\text{calc}}}{(\alpha_{\perp}/\alpha_{\parallel})_{\text{exp}}} \cdot 100$$

for the hydrogen molecule versus $\xi_{2p}(\text{H})$ (see Fig. 4) as indicators for the errors in the calculation of both properties.

From this plot an orbital exponent of 1.55 seems to be a good compromise to get improved IR as well as Raman intensities.

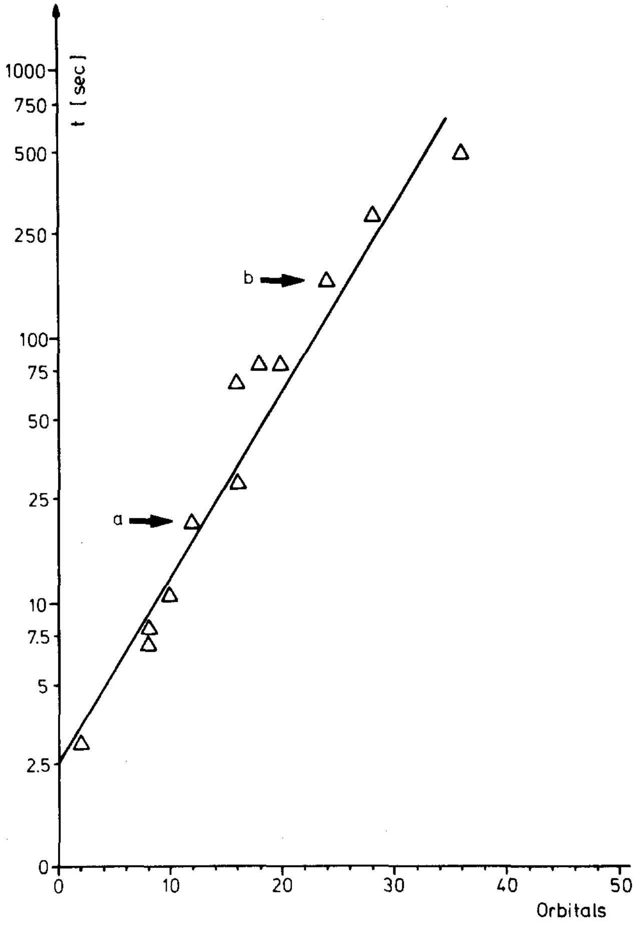

Fig. 3. Computing time for the intensities of one vibration as a function of the number of orbitals included in the calculation; for example: "a" ethylene calculated using the standard method and "b" using the method with extended basis set

Table 1. Dipole moments (in Debye) and polarizabilities (in 10^{-24} cm^3) for some small molecules

		Calculated values Standard CNDO/2				Extended CNDO/2				Experiment			
Molecule	Used geometry	μ	α_{xx}	α_{yy}	α_{zz}	μ	α_{xx}	α_{yy}	α_{zz}	μ	α_{xx}	α_{yy}	α_{zz}
H_2	r_{HH} 0.7403 Å	0	0	0	0.482	0	0.187	0.187	0.368	0	0.714	0.714	1.028[a]
N_2	r_{NN} 1.0976 Å	0	0.398	0.398	0.809	0	0.398	0.398	0.809	0	1.53_5	1.53_5	2.23_1[a]
HF	r_{HF} 0.917 Å	1.851	0.030	0.030	0.317	1.258	0.065	0.065	0.595	1.8195[b]	0.623	0.623	0.859[c]
H_2O	r_{OH} 0.960 Å ϕ 104.45°	2.145	0.107	0.607	0.241	1.367	0.157	1.062	0.591	1.8[b]	—	—	—[f]
HCN	r_{CH} 1.062 Å r_{CN} 1.157 Å	2.460	0.466	0.466	1.514	2.357	0.475	0.475	1.611	2.986[b]	1.92	1.92	3.92[d]
CH_4	r_{CH} 1.091 Å ϕ 109.47°	0	0.585	0.585	0.585	0	1.195	1.195	1.195	0	2.60	2.60	2.60[e]
C_2H_2	r_{CH} 1.0585 Å r_{CC} 1.2047 Å	0	0.328	0.328	1.895	0	0.420	0.420	2.120	0	2.87	2.87	4.73[e]
C_2H_4	r_{CH} 1.085 Å r_{CC} 1.339 Å ϕ_{HCH} 117.8°	0	1.092	0.489	2.446	0	2.047	0.665	2.879	0	—	—	—[g]

[a] Ref. [11]. [b] Ref. [4]. [c] Ref. [10]. [d] Ref. [14]. [e] Ref. [13]. [f] $\bar{\alpha}_{H_2O} = 1.44 \cdot 10^{-24}$ cm^3. [g] $\bar{\alpha}_{C_2H_4} = 4.22 \cdot 10^{-24}$ cm^3.

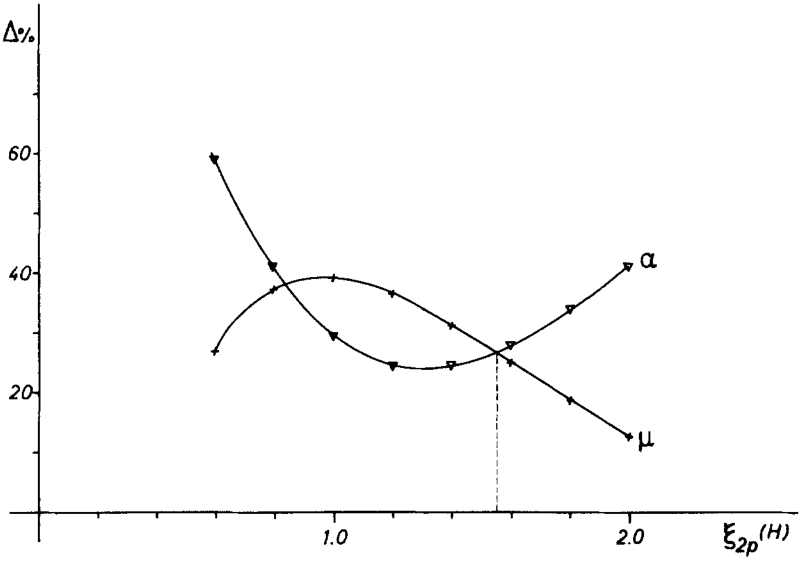

Fig. 4. Determination of the orbital exponent for the best simultaneous fit of IR and Raman intensities (see text)

3. Results and Discussion

Table 1 gives the results of the calculated dipole moments and polarizabilities for some small molecules in comparison to the values calculated by the standard CNDO/2 procedure and the experimental ones. The improvement of the results for the polarizabilities is proportional to the number of hydrogen atoms in a molecule. In the case of C_2H_2 there is good agreement between our value and that reported by Shinoda and Akutagawa [12] for the same basis set. The calculated dipole moments are worse than in the standard version (see text and Table 1).

As a test we calculated the IR and Raman intensities of ethylene. The calculated vibrational frequencies and normal coordinates are taken from a work of Ansmann [16]. The experimental and calculated frequencies as well as their assignments are listed in Table 2. Table 3 gives the calculated IR and Table 4 the Raman intensities. The experimental relative Raman intensities are calculated from the peak areas of the gas phase Raman spectrum. The spectral response of the spectrometer was taken into account. The resulting values for the totally symmetric bands are in fairly good agreement with the experimental intensity ratios from the Raman spectrum of solid ethylene given by Elliott and Leroi [18]. Thus we shall further use the values of these authors particularly for the bands at 3103, 1220 and 940 cm^{-1} whose intensities cannot be evaluated precisely enough from the gas phase spectrum.

One way to compare the calculated and experimental results is shown in Fig. 5, where we have plotted the "synthetic" spectra in relation to the experimental ones. Obviously this allows only a very rough qualitative estimation of the different

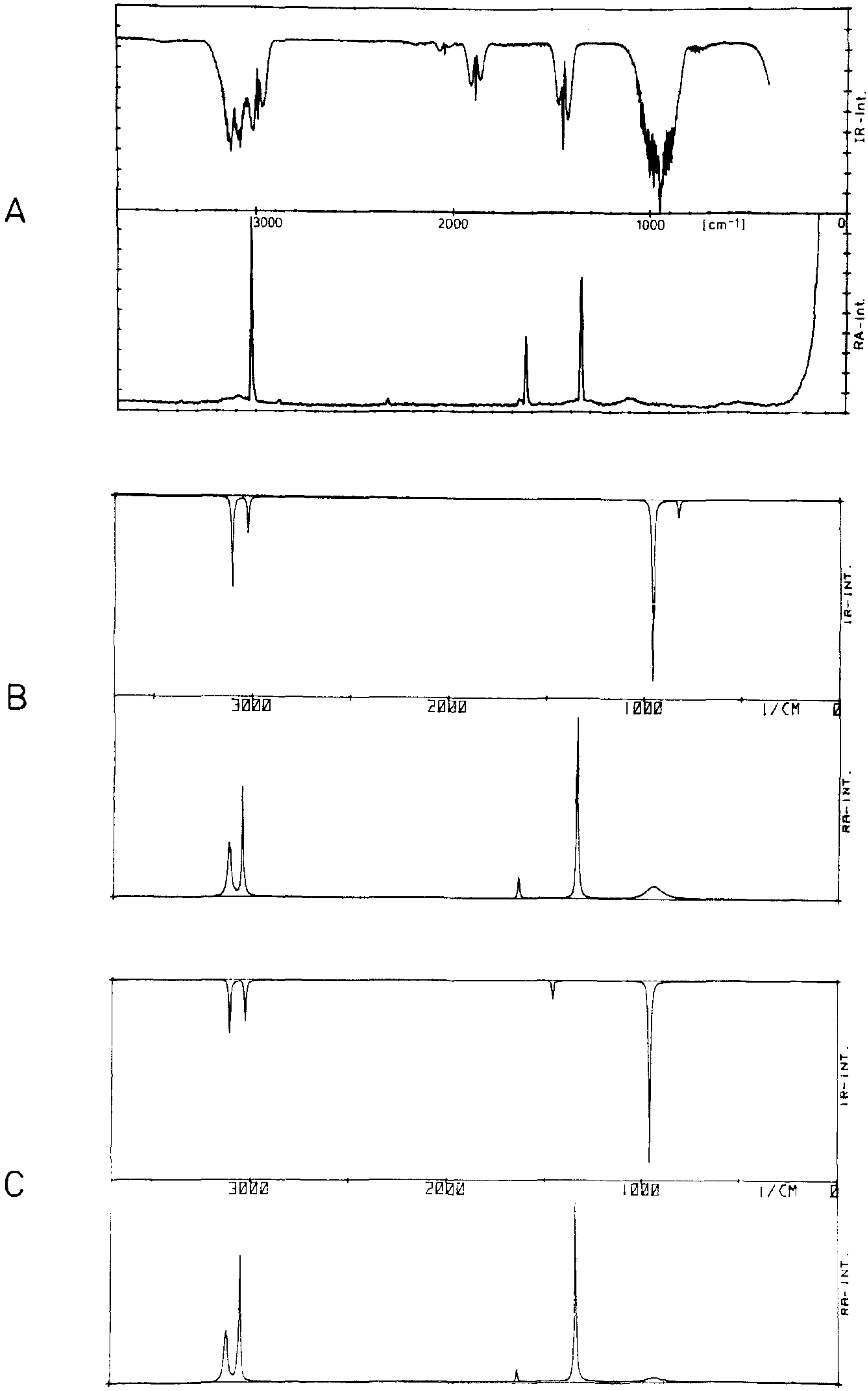

Fig. 5. Experimental (*A*) and "synthetic" (*B*, *C*) IR and Raman spectra of ethylene (*B* = standard CNDO/2; *C* = extended method using an orbital exponent $\xi_{2p}(\mathrm{H}) = 1.55$; the "synthetic" spectra are plotted using a Lorentzian function with constant half widths for the IR and experimental half widths of the bands for the Raman spectra; the areas below the curves correspond to the calculated intensity values)

Table 2. Experimental and calculated vibrational frequencies of ethylene

Symmetry species	$\tilde{\nu}_{\mathrm{exp}}$ (Ref. [15])	$\tilde{\nu}_{\mathrm{calc}}$ (Ref. [16])	Assignment
A_g	3026	3044	CH stretching
	1630	1635	C=C stretching
	1342	1336	CH_2 bending
A_u	1023	1023	C=C torsion
B_{1g}	3103	3112	CH stretching
	1220	1236	CH_2 rocking
B_{1u}	949	951	CH_2 out of plane
B_{2g}	940	944	CH_2 out of plane
B_{2u}	3105	3098	CH stretching
	826	819	CH_2 rocking
B_{3u}	3021	3020	CH stretching
	1444	1451	CH_2 bending

Table 3. Experimental and calculated IR intensities of ethylene

$\tilde{\nu}_{\mathrm{expt.}}$ (cm^{-1}) (Ref. [15])	A(10^{16} cm^2 mol^{-1} sec^{-1}) Expt. (Ref. [17])	Standard CNDO/2	ξ_{2p}(H) 1.0	ξ_{2p}(H) 1.55	ξ_{2p}(H) 2.0	Blom *et al.* (Ref. [19])
B_{1u} 949	23.928 ± 0.24	12.680	6.483	19.428	22.686	39.300
B_{2u} 3105	7.470 ± 0.19	20.316	33.181	18.286	0.931	11.700
826	0.159[a]	1.029	2.527	0.042	0.749	0.189
B_{3u} 3021	4.053 ± 0.20	7.874	33.871	13.647	1.322	7.050
1444	2.928 ± 0.02	0.109	0.595	2.941	3.314	2.520

[a] Error unknown, but assumed to be large

methods. Much more information follows from the absolute values listed in Tables 3 and 4.

It follows from the comparison of the standard deviation that for the IR intensities the improvement decreases in the order

$$\xi_{2p}(\mathrm{H})2.0 > \xi_{2p}(\mathrm{H})1.55 > \text{standard CNDO/2} > \xi_{2p}(\mathrm{H})1.0$$

and for the Raman intensities we find

$$\xi_{2p}(\mathrm{H})1.0 > \xi_{2p}(\mathrm{H})1.55 > \xi_{2p}(\mathrm{H})2.0 > \text{standard CNDO/2}.$$

A comparison of the values from different authors in Table 4 cannot be done without difficulties due to the fact that

1) different definitions of the Raman intensities are used (our intensities calculated with a factor 7/45 γ'^2 in Eq. 2 are comparable to experimental values obtained with linear polarized incident light, while intensities computed with a factor

Table 4. Experimental and calculated Raman intensities of ethylene

Symmetry species	$\tilde{\nu}_{exp}$ (cm^{-1}) (Ref. [15])	I/I_{3026} Experimental Gas (this work)	Solid (Ref. [18])	Matrix	Calculated This work Standard	ξ_{2p} 1.0	ξ_{2p} 1.55	ξ_{2p} 2.0	Other authors (Ref. [19])	(Ref. [20])	(Ref. [21])
A_g	3026	1	1	1	1	1	1	1	1	1	1
	1630	0.30	0.389[a]	0.572	0.197	0.078	0.097	0.160	0.175	0.245	0.10
	1342	0.53	0.812[a]	2.066	1.647	0.986	1.447	1.673	0.461	0.347	1.36
B_{1g}	3103	0.2	0.399	0.624	0.977	0.596	0.809	0.921	0.379	0.918	0.59
	1220	0	0.007[a]	—	0.001	0.021	0.001	0.001	0.007	0	0.03
B_{2g}	940	0.1	0.157[a]	0.442	1.220	0.020	0.393	0.932	0.174	0.082	0.05

[a] Sum of the intensities of two bands arising from crystal splitting.

13/45 γ'^2 (Blom [19] and Komornicki [20]) must be compared to spectra recorded using natural light as a source),
2) the normal coordinates are obtained from different force fields,
3) the geometries used show significant differences and the intensity calculation is known to be very sensitive to the normal coordinates as well as the geometries.

Nevertheless there is an overall agreement in the intensity values of the Raman bands of the different authors except of the bands at 1342 and 940 cm^{-1}. In comparison with the experimental values listed in the third column of Table 4 the intensity of the band at 940 cm^{-1} is overestimated in our calculations with the standard version and with the extended version using an orbital exponent of 1.55 or 2.0. The calculation with an orbital exponent of 1.0 yields a much better value. The Raman intensity of the CH_2-scissoring vibration (1342 cm^{-1}) is overestimated by all cited authors except Blom [19] and Komornicki [20]. Generally their *ab initio* calculations lead to better agreement with the experimental intensities.

However, a comparison with the intensity values reported by Elliott and Leroi [18] for matrix-isolated ethylene shows that the band at 1342 cm^{-1} is much better reproduced by our calculations and the calculation of Bleckmann [21]. The best way to find out the efficiency of the known computing methods would be the comparison of calculated and experimental absolute intensities. Up to now there are known many experimental absolute IR intensities but only very few absolute Raman intensities. Therefore much work has to be done mainly in the determination of absolute Raman intensities in order to get a better check on the method of calculation.

In general, the method with extended basis set leads to improved intensity values compared to the standard CNDO/2 version while needing significantly less computer capacity than the *ab initio* calculations.

Anyway it seems that this method in the present form can be used to improve doubtful assignments and to select the best vibrational force field for one substance, particularly for large organic molecules.

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