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A new aromatic probe — The ring stretching vibration Raman spectroscopy frequency

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ABSTRACT

A new aromatic criterion is presented to determine the aromatic degree of the high symmetric molecules. Group theory is used to explain the correlation between the aromatic degree and the value of Ring Stretching Vibration Raman Spectroscopic Frequency (RSVRSF). The calculations of the geometrical optimization, nucleus-independent chemical shifts (NICS) and values of the Raman Spectroscopy for the aromatic molecules—L_nH_n ($L = C$, Si, Ge, $n = 3, 5–8$) were performed using the Density Functional Theory (DFT) Method, as well as the correlations between the values of their RSVRSF and NICS values by Statistic Package for Social Science (SPSS17.0). There are high positive correlations between the theoretical calculated the NICS values and the value of the RSVRSF (A_{1g}/A_1') of the L_nH_n ($L = C$, Si, Ge, $n = 3, 5–8$). The bigger the aromatic degree, the bigger the RSVRSF is. The value of the RSVRSF is a new probe of aromaticity. Expectedly, it is predicted that the experimental determination of the aromatic degree can be achieved by the determination of the ring stretching vibration (A_{1g}/A_1') Raman spectrum frequencies for the aromatic target molecules.

1. Introduction

Aromatic degree of molecule depends on its stability (energy), structure (geometry), chemical reactivity, and spectroscopic properties [1]. However, most investigations on aromaticity based on the calculations rather than the quantitative measurements.

Experimentally, most of researchers analyzed the molecule structures by spectroscopy. Experimental bond lengths were used to evaluate the HOMA (harmonic oscillator measure of aromaticity) index of aromaticity [2]. The HOMA is defined as a normalized sum of squared deviations of the individual experimental (or calculated) bond lengths and an optimal bond length [3]. Limitation of the geometry-based HOMA approach: it cannot be directly measured [4].

A recent creditable calculation method for the molecular aromatic degree is nucleus-independent chemical shifts (NICS) [5] proposed by Schleyer. Significantly negative NICS values denote its diatropic ring currents and aromatic, while the positive values denote paratropic ring currents and anti-aromatic behavior. The zero NICS value denotes no-aromatic [6]. NICS only shows a modest dependence on the ring size [7]. NICS gains popularity as an easily computed and generally applicable criterion to characterize the aromatic degrees of the organic molecules [8], the inorganic aromatic molecules [9], all metal series [9–10] and the sandwich aromatic matching molecules [5,11,12,13]. NICS indices correspond to the negative of the magnetic shielding computed at ring centers (nonweighted mean of the heavy atom coordinates) with available quantum mechanics programs. In this rate, all kinds of vibration frequencies (including NMR) related the virtual atom can't be determined experimentally, NICS is only a theoretical aromatic index, not an experimental aromatic probe.

Up to this time, studies evaluated degree of π-delocalization in oligomers [14,15,16] and ions [17] by inspecting how the Raman frequency of breather mode (Ring Stretching Vibration Raman Spectroscopy Frequency) change with increasing chain length and the ions size. Recently, Kalescky [1] described anthracene and phenanthrene of aromaticity with the help of vibrational spectroscopy. Relative bond strength orders (RBSO) are obtained from the local stretching force constants. RBSO are used to establish an aromatic delocalization index AI. RBSO of the coupled cluster need larger basis sets, and calculation of anharmonicity corrections for the vibrational frequencies. So, it is difficult to determine aromatic of the coupled cluster by this aromaticity/antiaromaticity index. Raman frequencies can be measured to determine the degree of π-delocalization, not determine the degree of aromatic. Raman frequencies can be measured to determine the aromatic degree now that it can be measured to determine the degree of π-delocalization. Thus, it is very necessary to find an experimental aromatic probe by one kind of vibration frequencies.

In this study, we first study the relativity between the Ring Stretching Vibration Raman Spectroscopic Frequency (RSVRSF) and NICS, and then try to experimentally determinate the value of RSVRSF in order to find out an experimental aromatic probe. All geometries of target molecules were optimized. NICS and RSVRSF (A_{lg}/A_1') value of target molecules were calculated. We will described that the aromatic

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degree of target molecules must be related to the values of the RSVRSF (A_{1g}/A_1') and A_{1g}/A_1' normal vibration was a single, very strong scattering in the experimental and Raman spectrum calculation. We will demonstrate there are highly positive correlations between the aromatic degree of target molecules and the values of the RSVRSF (A_{1g}/A_1'). Thus it is possible to determine their aromatic degree by testing the values of the RSVRSF (A_{1g}/A_1') in experimentally and quantitatively.

2. Calculation and experiment methods

Four-membered ring have been shown to be destabilized by σ-antiaromaticity and are characterized by the paratropic values of NICS [18], We conducted the calculations for the geometry optimization, the values of the frequency and Raman spectroscopy of aromatic molecules — C_nH_n (n = 3, 5–8), Si_nH_n (n = 3, 5–8) and Ge_nH_n (n = 3, 5–8) — using calculation B3LYP/6–311 + g(d, p) method within Gaussian09 process package. Meanwhile, the NICS values of the researched series of molecules were calculated at the B3LYP-GIAO/6–311 + g(d, p) level. And the calculation results were shown in Table 1. Between the obtained the NICS values and the values of the RSVRSF, the correlation coefficients were investigated and then the relative curves were schemed. The natural bond orders of the bonding orbits for the various ground states were calculated with NBO 3.1. The NICS calculation value in the benzene ring center, NICS (0.0), is considerably consistent with the results by Schleyer et al. [19]. At the same time, the Raman spectrum of the analytical reagent benzene was obtained by the Raman spectroscopy NX RFT-RAMAN MODULE instrument at room temperature and atmospheric pressure (see Fig. 1). The result indicated that the relative error of the ring stretching vibration value (A_{1g}) is only 1.88% between our experimental value 993.1 cm^{-1} and calculated value 1011.8 cm^{-1} and the both values are close to 996.7 cm^{-1} reported in Ma et al.'s experiment [20]. It indicates that our method to calculate the Raman spectrum values for the aromatic target molecules is very reliable.

3. Results and discussion

(1) Experimental and calculated RSVRSF (A_{1g}/A_1').

The value of the Raman spectra (in Fig. 1) for the analytical reagent benzene was experimentally and theoretically determined before turning to our main calculation work. The experimental and calculated Raman spectrum shows a single, very strong scattering that mainly originates from the ring stretching vibration (A_{1g}).

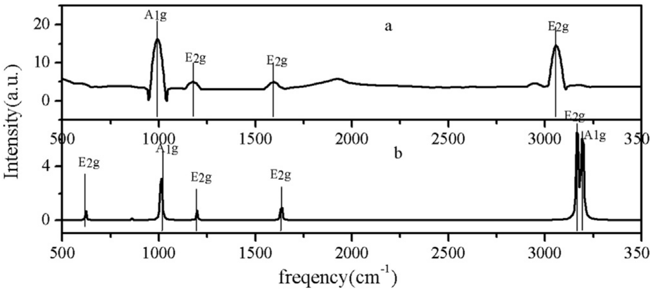

Fig. 1. The Raman spectrum of C_6H_6 (a) experimental determination and (b) theoretical calculation.

The Raman spectrum of C_nH_n (n = 3, 5–8), Si_nH_n (n = 3, 5–8) and Ge_nH_n (n = 3, 5–8) (in Fig. 2) shows a single, very strong scattering that originates from the A_{1g}/A_1' mode of the ring stretching. Therefore, it is promising to experimentally measure the value of the RSVRSF (A_{1g}/A_1') for these target molecules. The value of the strongest RSVRSF (A_{1g}/A_1') continuously downshifts with the ring size increasing: $C_3H_3^+$(1664.3 cm^{-1}), $C_5H_5^-$(1143.7 cm^{-1}), C_6H_6(1011.8 cm^{-1}), $C_7H_7^+$(874.4 cm^{-1}), $C_8H_8^{2+}$(753.1 cm^{-1}); $Si_3H_3^+$(604.7 cm^{-1}), $Si_5H_5^-$(436.6 cm^{-1}), Si_6H_6(380.4 cm^{-1}), $Si_7H_7^+$(325.5 cm^{-1}), $Si_8H_8^{2+}$(278.1 cm^{-1}); $Ge_3H_3^+$(336.7 cm^{-1}); $Ge_5H_5^-$(253.9 cm^{-1}), Ge_6H_6(221.9 cm^{-1}), $Ge_7H_7^+$(189.7 cm^{-1}), $Ge_8H_8^{2+}$(161.2 cm^{-1}).

(2) Correlation between the aromatic degree and the value of RSVRSF.

Target molecules D_{3h} ($C_3H_3^+$, $Si_3H_3^+$, $Ge_3H_3^+$); D_{5h} ($C_5H_5^-$, $Si_5H_5^-$, $Ge_5H_5^-$); D_{6h} (C_6H_6, Si_6H_6, Ge_6H_6); D_{7h} ($C_7H_7^+$, $Si_7H_7^+$, $Ge_7H_7^+$); D_{8h} ($C_8H_8^{2+}$, $Si_8H_8^{2+}$, $Ge_8H_8^{2+}$), are investigated employing the group theory method (see Table, in Supplementary material). We know that the target molecules all have the A_{1g}/A_1' vibration normal mode, A_{1g}/A_1' symmetry are Raman-active. The A_1'/A_{1g} symmetry is generated on the basis of the breather mode (Fig. 3). The A_{1g}/A_1' vibration normal is a single, very strong scattering in the experimental and calculation Raman spectrum. We explored the correlation between the aromatic degree and the target molecules the values of the RSVRSF (A_{1g}/A_1').

Table 1
The theoretical calculation data of the RSVRSF (A_{1g}/A_1')(cm^{-1}), molecule bond orders (MBO), force constants, bond lengths and aromatic degree (NICS)(ppm)of C_nH_n (n = 3, 5–8), Si_nH_n (n = 3, 5–8) and Ge_nH_n (n = 3, 5–8).

System	RSVRSF(A_{1g}/A_1') Freq[a](cm^{-1})	N_{imag}[b]	NICS (0.0)[c](ppm)	NICS (min)[d](ppm)	Bond	MBO	Force constants
$C_3H_3^+(D_{3h})$[f]	1664.3	0	−22.9	−28.6 (0.5)[e]	1.362	1.65	7.5
$C_5H_5^-(D_{5h})$	1143.7	0	−12.6	−12.6(0.00)	1.415	1.28	4.5
$C_6H_6(D_{6h})$	1011.8	0	−8	−10.5(0.75)	1.394	1.11	3.6
$C_7H_7^+(D_{7h})$	874.4	0	−6.2	−9.5(1.00)	1.396	0.83	2.8
$C_8H_8^{2+}(D_{8h})$	753.1	0	−6.8	−9.0(1.00)	1.408	0.7	2.1
$Si_3H_3^+(D_{3h})$	604.7	0	−20.9	−20.9(0.0)	2.202	1.56	2.8
$Si_5H_5^-(D_{5h})$	436.6	4	−17.2	−17.2 (0.0)	2.228	1.13	1.6
$Si_6H_6(D_{6h})$	380.4	1	−12.1	−12.1 (0.0)	2.216	1.01	1.2
$Si_7H_7^-(D_{7h})$	325.5	2	−9.3	−9.3 (0.0)	2.225	0.88	0.9
$Si_8H_8^{2+}(D_{8h})$	278.1	3	−7.6	−7.7 (0.5)	2.244	0.72	0.7
$Ge_3H_3^+(D_{3h})$	336.7	0	−18.3	−18.3 (0.25)	2.340	1.53	2.2
$Ge_5H_5^-(D_{5h})$	253.9	4	−16.8	−16.8 (0.0)	2.322	1.15	1.4
$Ge_6H_6(D_{6h})$	221.9	3	−12.5	−12.5 (0.0)	2.305	0.97	1.2
$Ge_7H_7^+(D_{7h})$	189.7	2	−10	−10.0 (0.0)	2.312	0.79	0.8
$Ge_8H_8^{2+}(D_{8h})$	161.2	3	−8.1	−8.1 (0.0)	2.333	0.65	0.6

[a] Ring stretching vibration (A_{1g}/A_1') Raman spectrum frequency.
[b] Imaginary frequency number.
[c] Ring center NICS value.
[d] Minimum NICS value.
[e] In the bracket, it is the position with the minimum NICS.
[f] In the bracket, it is molecular symmetry.