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The Raman Spectrum of the Squarate ($C_4O_4^{-2}$) Anion: An *Ab Initio* Basis Set Dependence Study

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O perfil de excitação Raman do anion esquarato, $C_4O_4^{-2}$, foi calculado por métodos *ab initio* no nível de teoria Hartree-Fock utilizando a Teoria de Resposta Linear (TRL) para seis frequências de excitação: 632,5, 514,5, 488,0, 457,9, 363,8 e 337,1 nm. Um total de cinco conjuntos de funções de base (6-31G*, 6-31+G*, cc-pVDZ, aug-cc-pVDZ e bases de Sadlej) foi investigado visando comparar o desempenho da base 6-31G*, em termos de convergência numérica dos resultados e custo computacional, com os dos demais conjuntos de base. Todos os conjuntos de base testados reproduzem as principais características do espectro Raman do anion esquarato no intervalo de excitação estudado. A base 6-31G* apresentou, em média, o mesmo desempenho nos resultados numéricos dos conjuntos de base maiores mas a uma fração do custo computacional mostrando-se apropriada para o estudo teórico dos derivados e complexos deste anion.

The Raman excitation profile of the squarate anion, $C_4O_4^{-2}$, was calculated using *ab initio* methods at the Hartree-Fock using Linear Response Theory (LRT) for six excitation frequencies: 632.5, 514.5, 488.0, 457.9, 363.8 and 337.1 nm. Five basis set functions (6-31G*, 6-31+G*, cc-pVDZ, aug-cc-pVDZ and Sadlej's polarizability basis set) were investigated aiming to evaluate the performance of the 6-31G* set for numerical convergence and computational cost in relation to the larger basis sets. All basis sets reproduce the main spectroscopic features of the Raman spectrum of this anion for the excitation interval investigated. The 6-31G* basis set presented, on average, the same accuracy of numerical results as the larger sets but at a fraction of the computational cost showing that it is suitable for the theoretical investigation of the squarate dianion and its complexes and derivatives.

Keywords: Raman spectra, squarate anion, vibrational spectroscopy, *ab initio* Linear Response Theory

Introduction

The advances in computer technology and theoretical methods over the last decades has made possible the *ab initio* calculation of molecular properties such as equilibrium geometries, infrared absorption intensities, vibrational frequencies and force fields for a large number of molecules and chemical systems of spectroscopic interest.[1] These calculated properties proved to be a valuable aid in the interpretation and assignment of the experimental spectroscopic data for a large number of molecules. However, in many cases, the peculiar electronic structure of the system being studied presents Raman spectroscopic features for which no routine computational methods are widely available. One of these cases is the squarate dianion ($C_4O_4^{-2}$), which belongs to the monocyclic oxocarbons ($C_nO_n^{-2}$, $3 \leq n \leq 6$) class of organic compounds with a wide range of applications. Since the first vibrational spectroscopic study by West and Ito,[2] the electronic, infrared and Raman spectra of the squarate anion as well as several of its complexes and derivatives have been the subject of several experimental and theoretical studies over the last decades (see, for example, the reviews by Santos[3] and Schleyer[4]). The Raman resonance and pre-resonance spectra of aqueous solutions of $C_4O_4^{-2}$ were studied by Ito *et al.*[5,6] in the 632-337 nm spectral range. The experimental excitation profiles obtained by these authors were interpreted theoretically in terms of the Jahn-Teller effect associated to the π,π^* electronic transition with the lowest doubly degenerated excited electronic state, and this effect was assumed to be the responsible for the intensity exhibited by the non-totally symmetric modes. As far as we know, no detailed *ab initio* calculations

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of the excitation profiles for this compound have been performed to date. While the calculation of static, or frequency-independent, Raman intensities has been made routine by almost all current *ab initio* packages, this is not the case for the computation of dynamic, or frequencydependent, Raman intensities. For resonant or near resonance Raman spectra, depending on the nature of the problem and following Hellers' methodology,[7,8] a series of techniques have been reported using single reference correlated calculations for the ground state mixed with *ab initio* or semi-empirical excited state calculations followed by numerical procedures to estimate the gradient of the excited electronic state energy surface with respect to each of the ground state's normal modes.[9-12] As pointed out by Hudson,[10] one of the caveats of this method, is that it is necessary that there be only one electronic transition in the region of study in order to use the excited state calculation. A systematic approach for the computation of dynamic Raman intensities, nonetheless, has been recently proposed by Helgaker and coworkers.[13] Using the Linear Response Theory (LRT)[1,14,15] to compute the frequency-dependent polarizabilities, these authors developed a Hartree-Fock and MCSCF formalism, and a computational implementation where the calculation of Raman intensities, within the Placzek polarizability theory,[16] involves the differentiation of the frequency-dependent polarizabilities, computed at the laser excitation frequency with respect to nuclear displacements. Although, basis set requirements for the computation of static and dynamic polarizabilities have been the subject of recent studies, only few reports have dealt with Raman intensities calculations. Fleicher and Pulay, using B3LYP/6-31G* level of theory, obtained semiquantitative agreement for the gas phase Raman intensities and depolarization ratios of benzene and coronene.[17] In a study carried out by Halls and Schlegel,[18] it was found that the Sadlej[19,20] polarizability basis set yields the best static intensities quality with respect to the computational cost. These results agree with those previously reported by Van Caillie and Amos,[21] and by Dulskov and Sauer[22] for the calculation of static and dynamic polarizabilities of a range of small molecules using correlated and non correlated methods. On the other hand, earlier vibrational dynamic Raman optical activity (VROA) calculations conducted by Helgaker *et al*.[13] argued in favor of the aug-cc-pVDZ basis set in order to achieve numerical stability on the calculated Raman intensities and, at least, on the use of the aug-cc-pVTZ basis set to achieve Hartree-Fock limit quality on the vibrational frequencies. However, it has been pointed out that, these bases sets are far too large to be used in the calculation of dynamic Raman intensities for most of the systems of chemical and spectroscopic interest. In the methodology developed by Helgaker, the basis set chosen may impose a severe impact on the time needed to solve the iterative frequency response equations. In this method, the computation of the gradient of the polarizability requires a numerical differentiation with respect to the N nuclear positions demanding 2*3*N computations which results in a very high computational cost. Together, these factors can make the calculation of dynamic Raman intensities by this method unfeasible for medium sized molecules. With respect to the $C_4O_4^{-2}$ anion, a former *ab initio* study of the vibrational force field of the squarate anion conducted by Torii and Tasumi, using the 6-31G*, 6-31+G* and 6-31+G(df) basis sets, found that the basis set has little effect on the correct description of the geometric and vibrational parameters of this anion, and that these parameters were more sensitive to the selection of theoretical methods for taking electron correlation into account.[23] Although the squarate anion alone may be studied using theory levels higher than Hartree-Fock and using large bases sets, this is not the case for the majority of its derivatives and complexes for which experimental spectroscopic data is available. In most of these cases, the 6-31G*/Hartree-Fock level of theory represents the best compromise in terms of the computational cost and the quality of the results. Therefore, a survey of the performance of the 6-31G* basis set in terms of computational costs and numerical convergence of the intensities is needed.

Our primary goal in this work is to compare the performance of the 6-31G* basis set to the larger ones, at the Hartree-Fock *ab initio* level of theory, in the calculation of the gas phase excitation profiles of the squarate anion in order to investigate factors such as the computational cost and the quality of the results in terms of its numerical convergence. The inclusion of electronic correlation effects, albeit important for accurate semiquantitative results, will not be considered initially as we are concerned with how well Hartree-Fock calculations can predict dynamic Raman intensities over a wide spectral range of exciting frequencies. These results will serve as a guide to gauge future calculations of the excitation profiles of squarate anion derivatives and complexes.

This paper is organized as follows; in the next section, we detail the computational and theoretical methods as well the bases sets used. Then, we present an analysis of the observed computational demand for each of the basis sets. Next, a summary of the previous studies and a brief theoretical background of the Linear Response Theory as it relates to the computation of Raman intensities are presented, followed by a breakdown of the numerical results. An analysis in terms of the numerical convergence of the excitation profiles and the ability of the bases sets studied to qualitatively reproduce the main spectroscopic features of the squarate anion is presented. We close our discussion by inspecting how the theoretical calculations in the gas-phase can be related to the experimental data in condensed phases.

Computational Details

All computations were carried out with the Dalton electronic structure program.[24] For the sake of timing and computational resource comparisons, a cluster of FreeBSD/Athlon computers running at 700 MHz and equiped with 128Mbytes of RAM, 64 kbytes of cache level 1, 512 kbytes of level 2 cache, 200Mbytes of virtual memory and standard UDMA 66Mhz disk subsystem was used in all cases. The program was compiled with the GNU Fortran77 2.95.2 compiler and linked against the linear algebra optimized ATLAS library. The following criteria were applied for the basis set selection. To evaluate the importance of the diffuse functions in the calculation of dynamic Raman intensities, the Pople's 6-31+G* basis set was included in the study. Following Helgaker's VROA results,[13] we also selected two Dunning's double zeta correlation consistent bases sets, cc-pVDZ and aug-cc-pVDZ. In addition, due to its high success rate on predicting static polarizabilities,[18,21,22] the Sadlej polarizability basis set was also selected. All the basis sets were obtained from the latest versions available at the Extensible Computational Chemistry Environment Basis Set Database.[25] For each basis set, the molecular geometry was optimized without symmetry constraints and an analytical Hessian was computed at the stationary equilibrium point for later use in the Raman intensities computations. In order to investigate the behavior of each of the basis sets in this methodology at the Hartree-Fock level over a wide spectral range of excitation frequencies, the polarizabilities were computed at six experimental laser excitation frequencies, in the interval from 632.8 to 337.1 nm, the same as used by Ito and co-workers for the measurement of the Raman excitation profiles of this anion in aqueous solution.[5,6] A numerical differentiation using symmetric nuclear displacements of ± 0.0001 a.u. about the equilibrium nuclear positions was done in order to obtain the gradients of the polarizabilities at each exciting frequency. The wave function energy convergence threshold was set to 10^{-8} a.u. and the iterative response equations convergence threshold was set to 10^{-7} a.u. The resulting absolute intensities were normalized, following Ito methodology, with respect to the intensity of the ν_2 (a_{1g}) band at 632.8 nm excitation which was taken as unity.

Results and Discussion

Computational demand of the basis sets

We commence our discussion by focusing our attention on the elapsed wall times for the calculation of the Raman intensities for each of the basis sets. As reported in Table 1, it is clear that this method may impose severe limitations on the basis set choices for the calculation of Raman intensities even for medium sized molecules like the squarate anion and at the Hartree-Fock level of theory. If we take into account the relative sizes of the bases sets versus the time required to compute the excitation profiles, it seems that there is no direct relation between them. The explanation for this apparent discrepancy resides in the numerical iterative methods employed by the current computational implementation. Most of the computing time is associated with the resolution of the iterative linear response equations until a given numerical convergence threshold is reached. In addition to the usual bottlenecks and overheads associated with the use of large basis sets such as the disk access, this step is highly dependent on the number of simultaneous excitation frequency responses requested, on the basis sets employed for a given theory level and on the convergence thresholds applied both to the wave function and to the response equations. If we take these results as the only criteria for basis set selection, the Sadlej's and the aug-cc-pVDZ basis sets should be discarded without further considerations due to their very slow convergence speed of the response equations. These results shouldn't be extrapolated, though. In another study of the Raman excitation profiles of nitrosyl chloride at MCSCF level of theory, we found that the Sadlej's basis set has the fastest convergence rate, surpassing even the smaller cc-pVDZ basis set[26]. From the standing point of current experimental research being done with this molecule, however, these results show that survey computational studies at the 6-31G*/HF level of theory will provide results at a computational cost that is less than 50% that of the other basis sets considered. Given the reliability and success of this basis set in several studies involving geometry and frequency calculations we need

Table 1. Elapsed wall times for the computation of the Raman excitation profiles using different basis sets in hours:minutes (hh:mm)

Basis Set	Primitives	Contracted	Time (hh:mm)
6-31G*	216	112	14:49
cc-pVDZ	208	112	30:49
6-31+G*	248	144	48:20
aug-cc-pVDZ	280	184	110:14
Sadlej	384	192	517:21

to investigate, now, how it compares with the other sets with respect to the Raman intensities and excitation profiles.

Summary of results from previous experimental studies

The observed spectrum of the squarate anion in aqueous solution is dominated by three intense bands, ν_{10} at 647 cm $^{-1}$, ν_2 at 723 cm $^{-1}$ and ν_5 at 1123 cm $^{-1}$. These bands were unambiguously assigned, respectively, to the b_{2g} ring deformation, to the a $_{1g}$ totally symmetric CC stretching and to the b $_{1g}$ asymmetric CC stretching.[2,9] The main features of the spectra reported by Ito *et al* can be summarized as follows[5] . Even at the longer excitation wavelengths, ν_{10} and ν_5 have intensities comparable to the most intense band ν_2. When the excitation wavelength is changed from red towards blue, these three bands show great intensity enhancement, with predominance of ν_5 as the strongest band above 488.0 nm and with ν_{10} and ν_2 having approximately the same intensity in the near ultraviolet region. The strong enhancements observed for the three bands at the 337.1 and 363.8 nm excitation wavelengths were attributed to pre-resonance effects at the edge of the $\pi \rightarrow \pi^*$ ($A_{1g} \rightarrow {}^1E_u$) electronic transition. The possibility of resonance due to the forbidden, very weak, $n \rightarrow \pi^*$ ($A_{1g} \rightarrow {}^1E_g$) absorption occurring in the same spectral interval was discarded based on symmetry considerations that predict, also, the symmetry species b_{1g} and b_{2g} as the effective species in the Jahn-Teller effect. These results show resemblance with those reported by Santos *et al* for the solid sodium salt,[27] but, in Santos' *et al* work, even if no qualitative or semiquantitative numerical estimates of the relative intensities for these three bands in the solid state sodium were reported, their results show that in the Raman spectra of this salt the totally symmetric ν_2 band shows a weaker dependence on the exciting frequency in relation to the observed enhancements of the ν_{10} and ν_5 bands, being the weakest of the three bands for exciting lines in the 514.5 to 406.7 nm interval. An analysis of the salt spectra shows another feature that attracts our attention and contrasts with the spectroscopic behavior of this anion in different phases of aggregation; the asymmetric ν_9 (b_{2g}) CO stretching, that shows very little intensity enhancement in aqueous solution, presents, in the solid salt spectrum with, response to the exciting frequency which is comparable to that of ν_5.

Dependence of the calculated excitation profiles on the basis set

In this section, the computed intensities are analyzed in terms of basis set dependence of the numerical convergence of the results. How these results compare with the experimental data is discussed in the next section. The real part of the Linear Response Theory expression for the evaluation of the $\alpha_{a,b}$ *-th* element of the frequency-dependent polarizability tensor for an exact state[14] is given by:

$$\alpha_{a,b}(\omega_b) = -\langle\langle\mu^a;\ \mu^b\rangle\rangle_{\omega b} = \sum_{k>0}\left(\frac{\langle 0|\mu^b|k\rangle\langle k|\mu^a|0\rangle}{\omega_b + \omega_k} - \frac{\langle 0|\mu^a|k\rangle\ \langle k|\mu^b|0\rangle}{\omega_b - \omega w_k}\right) \quad (1)$$

where ω_b is the exciting frequency of the incident homogeneous periodic electric field and $\omega_k = E_0 - E_k$ denotes the energy difference between the exact eigenstate $|0\rangle$ of H_0 at t = -∞:

$$H_0|0\rangle = E_0|0\rangle \quad (2)$$

and those of the k -th residual exact eigenstates:

$$H_0|k\rangle = E_k|k\rangle \quad (3)$$

of the set $\{|0\rangle, |k\rangle\}$ of exact eigenstates of the non interacting unperturbed system. Although for the Hartree-Fock method the ground state is the best variational approximation to the eigenstate $|0\rangle$, the remaining excited states are not accurate representations of the $\{|k\rangle\}$ set of excited eigenstates of the system for the evaluation of the expected values of the dipole transition matrix elements $\langle 0|\mu^i|k\rangle$ and $\langle k|\mu^i|0\rangle$ between the reference state $|0\rangle$ and the excited state $|k\rangle$. At the same time, different basis sets will produce different sets $\{E_k\}$ of eigenvalues affecting the denominators $(\omega_b \pm \omega_k)$ in the summation in equation 1. In the particular cases where the basis set yields virtual states for which $\omega_b \cong \omega_k$, the terms:

$$\frac{\langle 0|\mu^a|k\rangle\langle k|\mu^b|0\rangle}{\omega_b - \omega_k} \quad (4)$$

will have a very significant weight in the summation in equation 1 enhancing the frequency dependency of the molecular polarizability. These two factors characterize the basis set dependence of the calculation of the frequency-dependent polarizability tensor from the standpoint of Linear Response Theory. Raman bands, on the other hand, derive part of their intensities from the magnitude of the variation of the polarizability tensor with each normal mode of vibration, $(\partial\alpha / \partial Q_i)$. Unless the $\{E_k\}$ set of eigenvalues has a very strong dependence on the nuclear positions for very small nuclear displacements, like those used in this work, we should not expect significant changes in the $(\omega_b \pm \omega_k)$ denominators due to numerical differentiation. For a given exciting frequency we should expect, instead, that the behavior of the transition dipole elements with respect to the nuclear displacements, due to symmetry changes, will determine the basis set dependence of the intensities.

After these considerations, we turn our attention to the results. The calculated normalized gas phase intensities as well as the aqueous solution experimental results of the two measurements carried out by Ito are summarized in Table . In overall, and in accordance with the experimental evidence, all basis sets correctly predict an enhancement of the intensities as the exciting line wavelength varies from red to blue with a dramatic intensification effect for wavelengths below 457.9 nm. In the UV region, the spectra are dominated by the v_5 (b_{1g}) band at 1123 cm $^{-1}$ while the v_{10} (b_{2g}) band at 723 cm $^{-1}$ shows weaker intensity ratios as observed experimentally in aqueous solution. The calculated intensity ratios exhibit larger values than the experimental ones by factors that vary from 1.3 up to approximately 6.0 in the UV region of excitation. In the 632-457.9 nm excitation spectral interval all basis sets produce similar numerical results, with the exception of Sadlej's basis. The calculated intensity ratios for the totally symmetric v_2 (a_{1g}) band shows an average deviation of 0.06 among all the basis sets, while for v_{10} (b_{2g}) band this value reduces to 0.04 showing fast basis set convergence for these two vibrational modes. For the v_5 (b_{1g}) band, however, the basis sets with diffuse functions show an increase in the response to the exciting frequency. To inspect in more detail the observed behavior, the vertical energies of the first low lying E_u excited states and the corresponding oscillator strengths were computed at the equilibrium geometry using the Linear Response Theory within the Random Phase Approach (RPA) for each of the basis sets. These results are summarized in Table 3. An analysis of the energies displayed in this table shows that the basis sets without diffuse functions produce excited states 1^1E_u and 2^1E_u that are far from the energy of the higher exciting frequencies used in the calculations (see Table 2) reducing the contribution of these states to the summation in equation 1. For the basis sets with diffuse functions, on the other hand, this situation changes drastically; the three low lying excited states are very near

Table 2. The observed and calculated wavelength dependent Raman intensities of the squarate ion. The Raman intensity of the 723 cm $^{-1}$ line at 632.8 nm excitation is taken as 1.0

Excitation Wavelength (nm) Energy (eV)	632.8 1.960	514.5 2.410	488.0 2.536	457.9 2.708	363.8 3.408	337.1 3.678
v_{10} (b_{2g}) 647 cm^{-1}						
6-31G*	0.32	0.99	1.34	2.01	10.95	22.4
cc-pVDZ	0.31	0.95	1.29	1.93	10.61	21.8
6-31+G*	0.28	0.87	1.18	1.79	7.68	21.6
aug-cc-pVDZ	0.29	0.89	1.21	1.82	10.20	21.2
Sadlej	0.31	0.27	1.30	1.95	10.59	21.2
Experimental[6]	0.70	0.88	1.21	1.31	3.20	6.60
Experimental[5]	0.93	0.95	0.95	1.20	3.40	6.10
v_2(a_{1g}) 723 cm^{-1}						
6-31G*	1.0	2.92	3.88	5.68	27.6	53.9
cc-pVDZ	1.0	2.91	3.93	5.66	27.5	53.7
6-31+G*	1.0	2.95	3.95	5.85	21.1	52.8
aug-cc-pVDZ	1.0	2.87	3.79	5.48	31.9	53.7
Sadlej	1.0	2.63	3.28	4.10	29.7	49.3
Experimental[6]	1.0	1.19	1.41	1.62	3.6	7.9
Experimental[5]	1.0	1.0	1.0	1.4	3.6	6.6
v_5(b_{1g}) 1123 cm^{-1}						
6-31G*	0.58	2.66	3.71	5.80	37.67	82.3
cc-pVDZ	0.70	2.41	3.36	5.28	34.62	76.1
6-31+G*	0.94	3.21	4.47	7.00	45.40	74.8
aug-cc-pVDZ	0.94	3.19	4.44	6.94	45.18	99.6
Sadlej	1.19	4.05	5.65	8.84	58.65	131.2
Experimental[6]	0.98	1.54	1.78	2.14	6.00	14.3
Experimental[5]	0.71	1.0	1.30	1.80	6.70	13.0

1 eV = 1.602177 10^{-19} J

Table 3. HF/RPA vertical excitation energies (in eV; 1 eV = 1.602177 10^{-19} J) and oscillator strengths of the squarate anion of three low lying ^1E_u electronic states

	1 ^1E_u	2 ^1E_u	3 ^1E_u
6-31G*	5.60/0.433	10.56/0.159	12.75/0.001
cc-pVDZ	5.58/0.414	10.56/0.154	12.25/0.001
6-31+G*	5.29/0.119	5.39/0.069	5.73/0.334
aug-cc-pVDZ	4.87/0.030	5.03/0.018	5.56/0.468
Sadlej	4.38/0.013	4.55/0.027	5.49/0.477

to each other and nearer to the energies of the exciting frequencies than the states generated by the other basis sets and this results in higher sensitivities of these sets to the exciting frequencies used in the computation of the Raman intensities. This condition is more dramatic for Sadlej's basis sets where all three states have significant weights as compared to the remaining basis sets. Of the three normal modes investigated, the nuclear displacements associated with the ν_5 (b_{1g}) vibration produce, for all the basis sets, the strongest variation of the transition dipole matrix elements resulting in stronger enhancements as compared to the remaining vibrational modes.

The results can be summarized as follows: all basis sets reproduce the main features of the observed spectra of the squarate anion in aqueous solution at different excitation wavelengths. The excitation profiles associated with the ν_2 (a_{1g}) and ν_{10} (b_{2g}) vibrational modes show very little dependence on the basis set if compared to the ν_5 (b_{1g}) mode. RPA calculations of the vertical excitation energies at equilibrium geometry with different basis may precede Raman calculations to define their relationship with respect on the excitation frequencies to be employed in the study of the system of interest. The 6-31G* basis set yields intensity ratios of quality comparable to those returned by larger basis sets.

Theoretical versus experimental Raman excitation profiles

In the previous section we investigated the Raman excitation profiles of the three most intense bands of the squarate anion in gas-phase with respect their dependence to the basis set and, now, it is worth to query how these results relates to the observed profiles in aqueous solution. Despite the large amount of experimental data and the body of theoretical investigations of this anion and its derivatives there are very few structural studies of the squarate anion in aqueous solution. Raman bandshape analyses conducted by Ribeiro *et al* strongly suggest the existence of structurally well-defined water cages such as those formed via hydrogen bonds with the oxygens of the solute.[28] Molecular dynamics and quantum *ab initio* studies carried out by Martins[29,30] to investigate the structure of the first solvation shell found a well-defined structure consisting of approximately 18 water molecules around the anion with about 12 of these molecules tightly bonded to the oxygens forming a highly symmetric solute-solvent structure. The *ab initio* results pointed out in the direction of a solute whose electronic structure is not considerable affected in the presence of the solvent, making, in principle, conceivable a correlation between the theoretical calculations in the gas phase and the results in aqueous solution. Indeed, if we compare the trends of the theoretical excitation profiles for the squarate anion with those reported for aqueous solution by Ito and those measured in the solid state by Santos we find a better resemblance between the gas phase results with those obtained in water solutions. Figure 1 depicts the simulated Raman spectra using the experimental Raman intensity ratios from Ito[6] and the computed intensity ratios at 6-31G*/HF level of theory. The curves were produced with the Spectrum[31] program using a half-width of 10 cm $^{-1}$ for the three bands. A visual inspection of Figure 1 shows that the theoretical results reproduce, approximately, the pattern of the observed spectra in aqueous solution. This comparison is valid inasmuch as we take into consideration a series of limitations associated with both the experimental and theoretical methods employed. According to Myers, Raman intensity measurements are accurate to no more than ± 10-15% even in the best cases.[32] The difficulties associated with the measurement of the excitation profiles of the squarate anion in aqueous solution can be estimated by contrasting, in Table 2, the two measurements made by Ito *et al* in 1975 and 1978 where deviations of the intensity

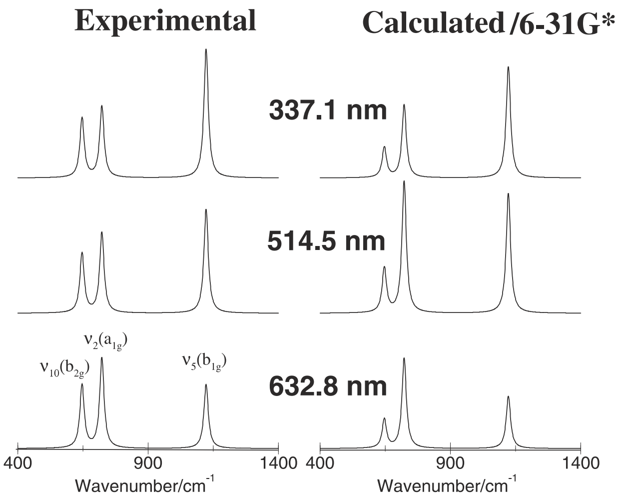

Figure 1. Simulated Raman spectra of the squarate anion in aqueous solution using the observed[6] and calculated relative intensities for three exciting lines.

ratios of up to 60% are observed. At the same time, the theoretical methods employed in this study, as discussed, are very dependent on an appropriate description on the excited states. A better description can be achieved by the inclusion of static electronic correlation via MCSCF wave functions but this implies the use of appropriate correlation consistent basis sets and the accurate definition of the active space[33] in order to take into account all states associated with Raman enhancement with a significant increase in the computational costs. Small active spaces for high symmetry compounds will result in relatively fast calculations but only those states included will be correctly described. The inclusion of dynamic correlation via a single configuration reference state such as MP2/SOPPA[34] or coupled cluster LRT[35] are out question for current computational resources for most of the derivatives of this molecule.

Conclusions

In this work, the gas phase *ab initio* pre-resonance profiles for the squarate anion computed at the Hartree-Fock level of theory are reported for the first time. The basis set dependence of the intensities is related both to the sensitivity of the transition dipole matrix elements to the normal modes and to the spectrum of vertical excitation energies produced by each of the basis sets. The overall features of the calculated spectra are in excellent agreement with the experimental data. Our results show that *ab initio* calculations conducted at the 6-31G*/HF level of theory produce numerical results comparable to those obtained with larger basis sets at a fraction of the computational cost in the spectral range of laser exciting lines investigated. The squarate anion has a peculiar electronic structure that requires the inclusion of electronic correlation effects in the description of the excited states that contribute to the Raman intensities. We have no doubt that further theoretical studies where these effects are taken into account in the computation should bear better results. Unfortunately, such kind of investigation is currently out of reach for our computational resources. We hope this work will stimulate further experimental and theoretical investigations of the Raman excitation profiles of the squarate anion, and its derivatives.

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