Ab initio spectrograms of the molecular vibrational spectrum

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Theoretical spectrograms of the vibrational spectrum of 3,3-dimethylcyclopropene were constructed and juxtaposed with the experimental Raman and IR spectrograms. The theoretical spectrograms are represented as sets of vertical lines starting from the points corresponding to the values of the vibrational frequencies calculated from the scaled quantum-mechanical (QM) force field obtained at the HF/6-31G*//HF/6-31G* level. Two theoretical Raman spectrograms were constructed. In the first case, the heights of the vertical lines correspond to the QM values of the Raman scattering activities. In the second case they represent the relative differential Raman cross-sections calculated using the QM values of Raman scattering activities. The initial vibrational mode matrix remains virtually unchanged upon scaling of the QM force constant matrix because the dispersion of the scale factor values is low. Therefore, the heights of the theoretical lines for the IR spectrogram represent the QM intensities directly. The theoretical spectrogram based on the relative differential Raman cross-sections was shown to depict the experimental Raman spectrum more adequately. This makes it possible to use the results of the corresponding QM calculations more completely and obtain well-substantiated assignments of the vibrational frequencies.

Key words: quantum-mechanical force field, intensities of Raman lines and IR absorption bands, 3,3-dimethylcyclopropene.

Vibrational spectroscopy is an experimental method for the investigation of molecular structure. The study of molecular vibrational spectra permits determination of the molecular symmetry as well as the detection of the presence of particular functional groups. Computational vibrational spectroscopy plays a key role in obtaining these results. The advancement of quantum-mechanical computation techniques[1] has brought about a break with the traditional philosophy of calculational vibrational spectroscopy.[2—5]

The unconventional construction of the theoretical spectrogram of a molecular vibrational spectrum of a large molecule involves quantum-mechanical calculations of the force field and its scaling according to Pulay[6—8] using the scale factors (SFs) obtained for well characterized small molecules with the same structural fragments. This procedure gives the corrected theoretical vibrational frequencies, which are close to the experimental values. At the same time the results of the quantum-mechanical calculations using any program from the GAUSSIAN series[9] provide, for each *j*th normal vibration, the calculated values of the IR intensity and the Raman scattering activity, S_j.[10] However, the latter is, generally speaking, not the intensity of the corresponding line of the Raman spectrum (see below). Therefore, the aim of this work is to demonstrate the advantages of using the relative differential Raman cross-sections rather than the Raman activities obtained from calculations with the GAUSSIAN programs[9] for assignment of bands in the vibrational spectrum.

Raman cross-sections

In the case under consideration we are concerned with normal Raman scattering, *i.e.*, excitation of Raman scattering in the frequency region widely separated from resonance. Intensities of lines in a Raman spectrum are known to be proportional to the Raman cross-sections, $d\sigma_j/d\Omega$, which can be calculated from the quantum-mechanical values of S_j (in Å^4 (amu)$^{-1}$). Indeed, the Raman activity, S_j, of the *j*th normal vibration is contained in the expression for the absolute differential Raman cross-section[10]:

$$\frac{d\sigma_j}{d\Omega} = \frac{(2\pi)^4}{45} \frac{(\nu_0 - \nu_j)^4}{1 - \exp\left(-\frac{hc\nu_j}{kT}\right)} \frac{h}{8\pi^2 c\nu_j} S_j, \qquad (1)$$

where ν_0 is the frequency of the exciting line; h, c, and k are universal constants; T is temperature; and σ_j and Ω are

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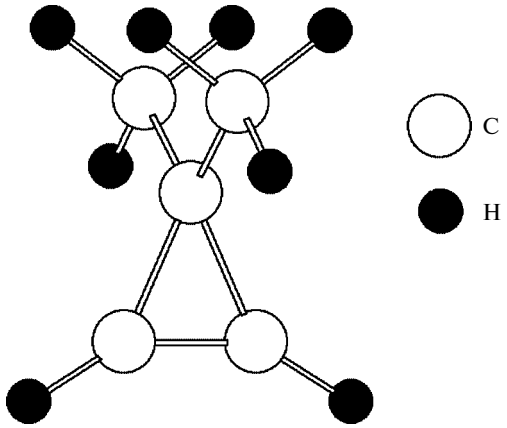

Fig. 1. Structural model of the 3,3-dimethylcyclopropene molecule (**1**).

respectively the scattering cross-section and the solid angle of light collection (in $Å^2$ sr^{-1} or in 10^{-16} cm^2 sr^{-1}). The Raman scattering activities are the linear combinations of squares of sums and differences of the first derivatives of the polarizability tensor with respect to the nuclear normal coordinates.[10]

To illustrate the necessity of conversion from S_j to $d\sigma_j/d\Omega$ when juxtaposing the experimental spectrogram with the theoretical one, we calculated the theoretical Raman spectrum of 3,3-dimethylcyclopropene (**1**, Fig. 1) at the HF/6-31G*//HF/6-31G* level. Earlier,[11] the Raman spectrum of molecule **1** was measured for a sample in the liquid phase (Fig. 2, *c*).

The spectrogram in Fig. 2, *b* reproduces the positions of the molecular lines with the theoretical vibrational frequencies of **1**, active in the Raman spectrum and calculated using the scaled quantum-mechanical force field. The heights of the vertical lines are proportional to the relative differential Raman cross-sections for the corresponding vibrations calculated using expression (1).

The spectrogram in Fig. 2, *a* corresponds to the same theoretical frequencies calculated using the scaled quantum-mechanical force field of molecule **1**,[11] but the heights of the vertical lines are now proportional to the Raman activities, S_j, taken directly from the GAUSSIAN[9] output.

Intensities of IR bands

The output of GAUSSIAN[9] contains the intensities of the vibrational bands active in the IR spectrum.[12,13] When scaling the quantum-mechanical force field, it is first converted from Cartesian coordinates into the internal valence independent coordinates. Then the $F^{q\text{-}m}$ matrix obtained is congruently transformed using a diagonal matrix of SFs (D), *i.e*,

$$F^{\text{scal}} = D^{1/2} F^{\text{q-m}} D^{1/2}.$$

If all elements of the diagonal matrix D take the same value (scalar matrix), after solution of the vibrational problem[14,15]

$$G^{\text{q-m}} F^{\text{scal}} L^{\text{scal}} = L^{\text{scal}} \Lambda,$$

the vibrational mode matrix obtained, L^{scal}, remains unchanged[16–18] compared to the vibrational mode matrix $L^{\text{q-m}}$ obtained by solving the secular equation

$$G^{\text{q-m}} F^{\text{q-m}} L^{\text{q-m}} = L^{\text{q-m}} \Lambda^{\text{q-m}},$$

where $G^{\text{q-m}}$ is the matrix of kinematic coefficients for the quantum-mechanical geometric parameters and Λ is the diagonal matrix of the frequency parameters related to the harmonic vibrational frequencies ω_k ($\lambda_k = s\omega_k^2$). The coefficient s depends on the choice of units of measurement. Thus, for the homogeneous scaling (equality of all SFs) one gets

$$L^{\text{scal}} = L^{\text{q-m}}. \qquad (2)$$

If Eq. (2) holds, the theoretical IR spectrogram can be constructed using the quantum-mechanical intensities given in the GAUSSIAN [9] output since the L^{scal} matrix is contained in the expression for absorption within the jth spectral band.

However, in most calculations involving scaling of the quantum-mechanical force fields, Eq. (2) is only nearly fulfilled because the elements of the diagonal matrix D slightly differ from one another. Nevertheless, if the dispersion of the SC values near the mean value is small, then

$$L^{\text{scal}} \approx L^{\text{q-m}}. \qquad (3)$$

This means that if expression (3) is valid, the theoretical IR spectrogram can also be constructed using the quantum-mechanical values of the band intensities.

For molecule **1** the dispersion of the SF values from their mean value is 0.0537 (without inclusion of the SF for the torsional force constants of the Me groups because these coordinates are almost completely "separated" from other coordinates in the L^{scal} matrix). Thus, expression (3) is valid for molecule **1** and the heights of the vertical lines in the theoretical spectrogram (Fig. 3, *a*) correspond to the relative quantum-mechanical intensities of the IR absorption bands.

Results and Discussion

Juxtaposition of the three spectrograms shown in Fig. 2 demonstrates significant differences between the relative Raman activities S_j (see Fig. 2, *a*) and the relative differential Raman cross-sections (see Fig. 2, *b*). At the same time reasonable agreement between the latter and the distribution of the relative experimental intensities of the lines in the Raman spectrum of molecule **1** is evident.

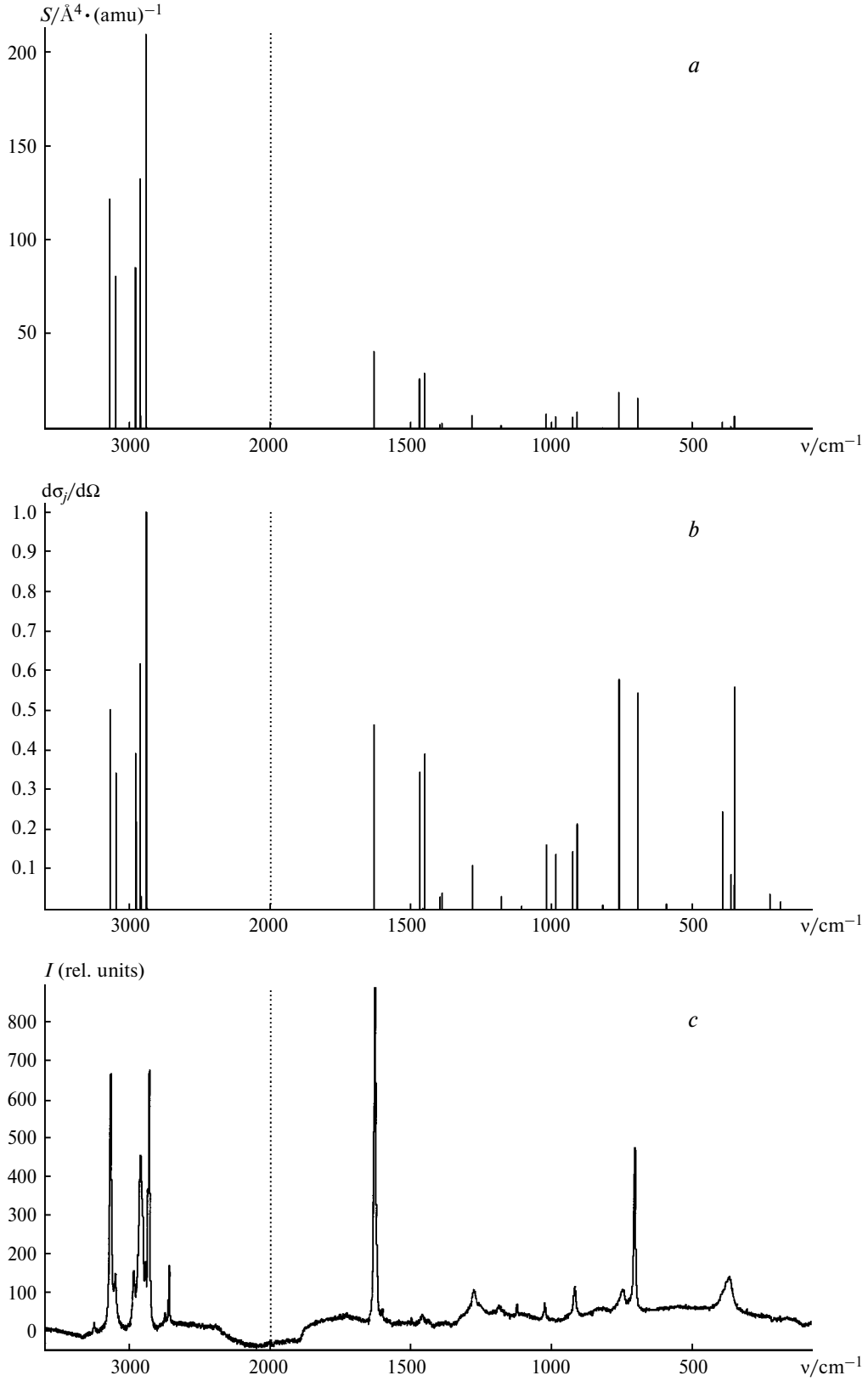

Fig. 2. Theoretical (*a*, *b*) and experimental (*c*) Raman spectrograms of 3,3-dimethylcyclopropene (**1**); *S* is the Raman activity and $d\sigma_j/d\Omega$ is the relative differential Raman cross-section.

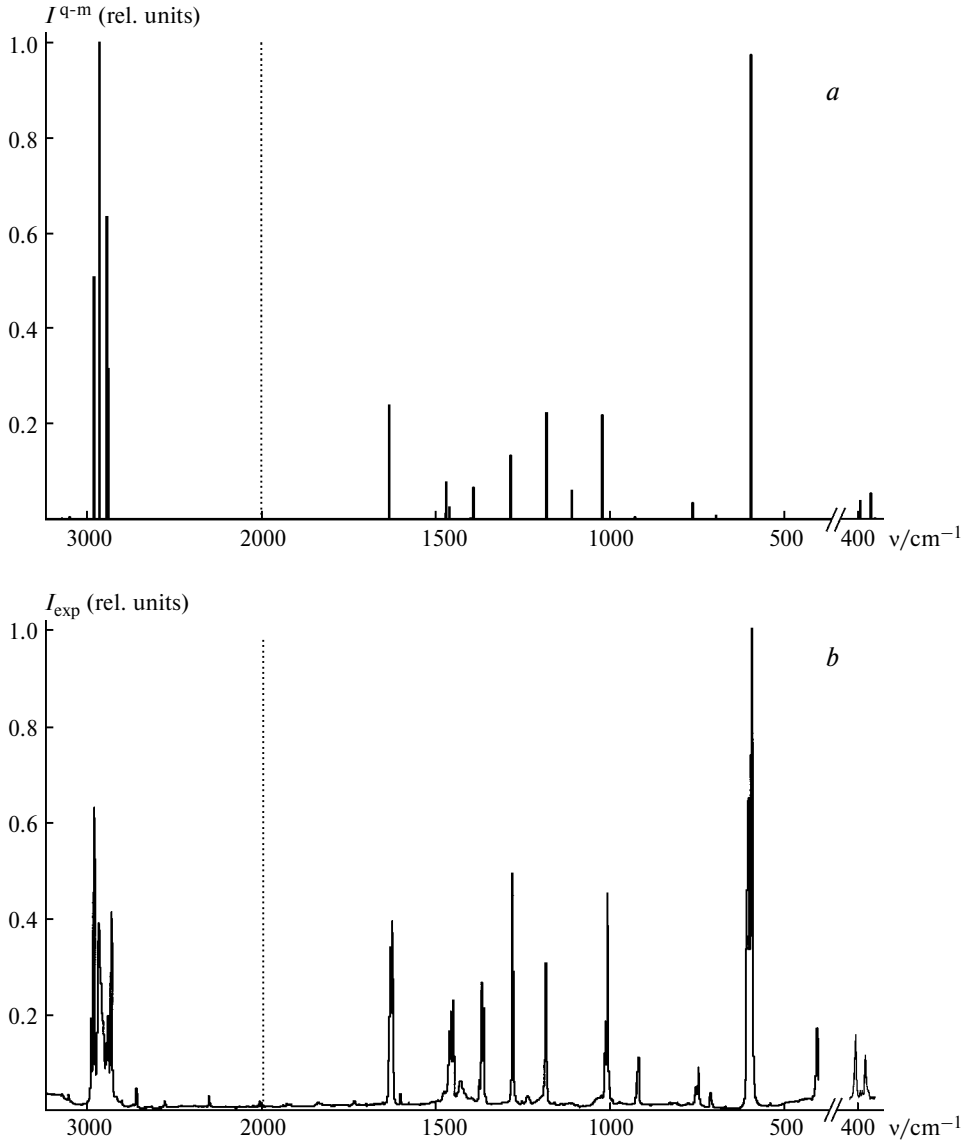

Fig. 3. Theoretical (*a*) and experimental (*b*) IR spectrograms of 3,3-dimethylcyclopropene (**1**).

One should also take into account the fact that some experimental lines in the Raman spectrum have a quite large halfwidth and that the experimental intensity is equal to the area under the line contour.

The example considered clearly indicates the necessity of conversion from the theoretical Raman activities obtained from quantum-mechanical calculations using the GAUSSIAN program[9] to the corresponding differential Raman cross-sections.

When constructing the theoretical Raman spectrogram, it is well to bear in mind the following. If we compare the results of quantum-mechanical calculations with the experimental data for a narrow spectral region, one can use the calculated quantum-mechanical Raman activities S_j. This immediately follows from examination of expression (1): if the difference between the frequencies ν_i and ν_j is small, the corresponding factors before S_i and S_j in expression (1) are approximately equal and the Raman cross-sections, $d\sigma_i/d\Omega$ and $d\sigma_j/d\Omega$, appear to be approximately proportional to the corresponding activities. This feature was used[11] in the assignment of the lines with close-lying frequencies in the Raman spectrum of molecule **1**. However, if the separation between ν_i and ν_j is rather large, it is necessary to use expression (1) and perform the corresponding conversion.

As can be seen in Fig. 3, the theoretical spectrogram (Fig. 3, *a*) simulates the pattern of the experimental IR spectrum of molecule **1** reasonably well. To avoid confusion, it should be pointed out that the experimental band at 404 cm^{-1} is present twice in the given spectrogram (see Fig. 3, *b*). In addition, it should also be noted that the experimental spectrum of molecule **1** shown in Fig. 3 was

recorded in the crystalline phase, so the contours of some bands are complicated by the Davydov splittings.

Nevertheless, conversion of the quantum-mechanical intensities for the vibrational bands active in the IR spectrum is also needed when scaling the force field if the dispersion of the SF values is large (*e.g.*, several tenths). In this case one can take advantage of the dipole moment derivatives with respect to the Cartesian coordinates (given in the GAUSSIAN program output). These derivatives should first be transformed into the corresponding derivatives with respect to the normal coordinates using the equation

$$\frac{\partial \mu_k}{\partial Q_i} = \sum_j \left(\frac{\partial \mu_k}{\partial X_j} \right) L_{ij}^{\text{scal}},$$

where μ_k is the component of the dipole moment in Cartesian coordinates, Q_i is the ith normal coordinate, and X_j is the Cartesian coordinate of the jth displacement. Next the IR intensities are converted using the expression

$$I_i = \frac{N\pi}{3c^2} \left[\left(\frac{\partial \mu_x}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_y}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_z}{\partial Q_i} \right)^2 \right].$$

Here I_i is the total integrated band intensity of the ith normal vibration Q_i; μ_x, μ_y, and μ_z are the components of the dipole moment in Cartesian coordinates, N is the Avogadro constant; and c is the speed of light.[19]

It should be noted that DFT calculations using, *e.g.*, the B3LYP approximation[20] usually give rather large deviations from experiment for one or more theoretical vibrational frequencies. The formal application of the scaling procedure to such force fields is bound to result in a significant modification of the vibrational mode matrix L^{scal} compared to the initial quantum-mechanical matrix $L^{\text{q-m}}$ due to a large dispersion of the SF values. Because of this, in order to compare the experimental intensities of the IR absorption bands with the theoretical values the latter should be converted taking into account the changes in the L^{scal} matrix. Besides, it should be noted that in the case of DFT calculations there is no systematic difference between the calculated and experimental vibrational frequencies. Therefore, applying the scaling procedure to the force fields found from DFT calculations cannot yield scale factors that could be transferred to related molecules.

The aforesaid is also true for the results of solution of the inverse vibrational problem using the quantum-mechanical force field as an initial approximation.[21—24] Criticism of such an approach is given in Refs. 2—5.

Some differences between the relative intensities of the widely separated lines in the theoretical and experimental Raman spectrograms are probably due to the level and basis set of the quantum-mechanical calculations.[1] The theoretical intensities of the Raman lines are determined by the derivatives of the molecular polarizability tensor with respect to the corresponding normal coordinate.[10] At the same time the experimental intensity of the corresponding line is governed by not only the changes in the molecular polarizability for a particular vibration but also some additional factors (see, *e.g.*, Ref. 25). The effect of the instrumental factors should also be mentioned.

The vibrational frequencies given in the spectrograms in Figs. 2, *a* and 3, *a* were calculated using the scaled force field. These frequencies can be rather closely situated with a consequent overlapping of the vertical lines simulating their relative intensities. However, the band overlap is also observed in the experimental spectrograms for the closely spaced bands. Owing to the minor difference between the calculated and experimental vibrational frequencies this sort of overlapping in the experimental spectrogram can be different from the overlapping in the theoretical spectrograms. This is most often observed in the region of the stretching vibrations of the C—H bonds (see Figs. 2 and 3).

Replacing the vertical lines by the bands with a distinct halfwidth prescribed by the assumed line shape (*e.g.*, a Lorentzian function) can serve as a final stage in construction of the theoretical spectrogram. However, such a modification of the theoretical spectrogram is not substantially significant when carrying out vibrational analysis of a sample.

Thus, the outlined theoretical spectrograms of the vibrational spectrum of molecule **1** offer an example of refined treatment of the results obtained in quantum-mechanical calculations of the force field and the results on the intensities of the vibrational bands. This is useful in obtaining more reliable information to perform vibrational analysis of a sample.

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