

mented STO-3G basis set is used but the these respective barriers are *higher* by 1.60 and 3.51 kcal/mol when the requisite augmented DH basis set is used.

A direct comparison of the calculated values of the corresponding heights in the isologues dimethyl diselenide and dimethyl disulfide might not be warranted for calculations based on the augmented or nonaugmented STO-3G basis sets inasmuch as the levels of refinement used for the bases of the Se and S atoms are quite different; furthermore, the set of functions used for the Se atom, namely, a primitive [12s,8p,2d] set contracted into a [6s,4p,2d] set, is much more extensive than the minimal basis set comprised of only three Gaussian functions that is used for the S atom. On the other hand, fairly extensive sets are used for both the Se and S atoms when the augmented DH set is used, and so a comparison of corresponding barrier heights might well be justified in this case.

We conclude that it is possible to calculate reasonable values of both cis and trans barriers in dichalcogen compounds, but it is difficult to decide on the basis of these calculations whether corresponding barrier heights are higher in the diselenide isologue or in the disulfide isologue¹⁹.

Acknowledgment. This work was supported, in part, by National Institutes of Health Grant AM-18399. V. R. is deeply indebted to Dr. Michel Dupuis, National Resource for Computation in Chemistry, University of California, Berkeley, CA for his aid in performing these calculations and for his poignant comments on this manuscript, to Dr. Harry F. King for his help with one of the references, and to Mrs. Sara W. Leake for her aid in preparing the manuscript.

Registry No. Dimethyl diselenide, 7101-31-7.

(19) Infrared and Raman spectroscopic data (ref 19a-c) and thermodynamic data (ref 19d) on dimethyl disulfide and dimethyl diselenide have been published. Although these data do contain information on barrier heights about the dichalcogen bridge, careful comparative studies of these two isologues have not, to our knowledge, been reported, and so it is not possible at present to decide on the basis of experimental studies whether corresponding barrier heights are higher in the disulfide or in the diselenide compound. (a) Scott, D. W.; Finke, H. L.; Gross, M. E.; Guthrie, G. B.; Huffman, H. M. *J. Am. Chem. Soc.* **1950**, *72*, 2424-2430. (b) Crowder, G. A.; Scott, D. W. *J. Mol. Spectrosc.* **1965**, *16*, 122-129. (c) Green, W. H.; Harvey, A. B. *J. Chem. Phys.* **1968**, *49*, 3586-3595. (d) Hubbard, W. N.; Douslin, D. R.; McCullough, J. P.; Scott, D. W.; Todd, S. S.; Messerly, J. F.; Hossenlopp, I. A.; George, A.; Waddington, G. *J. Am. Chem. Soc.* **1958**, *80*, 3547-3554.

Matrix Isolation Studies of Nucleic Acid Constituents. 2. Quantitative ab Initio Prediction of the Infrared Spectrum of In-Plane Modes of Uracil

Steven Chin, Ismael Scott, Krystyna Szczepaniak,[†] and Willis B. Person*

Contribution from the Department of Chemistry, University of Florida,
Gainesville, Florida 32611. Received August 3, 1983

Abstract: The dipole moment derivatives (or atomic polar tensors (APT's)) for the atoms in uracil have been calculated in an ab initio quantum mechanical calculation, using the GAUSSIAN 76 program with 4-31G basis functions. The frequencies and normal coordinate transformation matrices have been calculated from the force constants obtained from the ab initio quantum mechanical calculations by Nishimura et al. These are combined with our calculated APT's to predict absolute intensities and to give a prediction from ab initio calculations of the entire infrared spectrum for the in-plane modes of the isolated uracil molecule. This predicted spectrum is in excellent agreement with the experimental spectrum (from Szczepaniak et al.) of uracil isolated in a matrix. This result indicates that it is possible at present to make good quantitative predictions that are very useful in assignment and interpretation of vibrational spectra even for molecules that are as complicated as uracil. Comparisons are given between experimental and predicted spectra for matrix isolated uracil and for *N*₁,*N*₃-dideuterouracil, and the predicted spectra are also tabulated for C₅,C₆-dideuterated, N₁,N₃,C₅,C₆-perdeuterated, C₅-deuterated, C₆-deuterated, N₁-deuterated, and N₃-deuterated uracils. The calculated APT's are also tabulated for use in future predictions of intensities of other nucleic acid constituents by transferring APT's.

Recently, it has been shown that it is possible to predict with considerable accuracy the infrared absorption spectra of small molecules.¹⁻³ These predictions are made by using normal coordinate analyses based on force constants and intensity parameters transferred from related molecules or from ab initio quantum mechanical calculations. Comparisons between the experimental spectra and the predicted spectra for these molecules have shown that the predictions of absolute intensities can be expected to be in agreement with the experimental spectra within a "factor of two".⁴ While it may seem that the typical "factor-of-two" agreement that we expect between the predicted and experimental intensities may be too poor to be of any value, this magnitude of agreement is sufficient to be very useful to the experimental spectroscopist.⁴ It is important to realize that when the predicted spectral patterns (within a factor of two, or even three) are compared with an experimental spectrum (for example, see ref-

erence 4 or Figure 2 of this paper) the usual agreement is close enough to be "very good" and "quantitative" enough to be useful in several applications. For one thing, predictions of this type for species (such as *isolated* uracil molecules) which are difficult to obtain in a bottle⁵ are expected to be of considerable importance in the interpretation of experimental studies of these species in

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(2) (a) C. E. Blom, P. J. Slingerland, and C. Altona, *Mol. Phys.*, **32**, 1359 (1976). (b) C. E. Blom, and C. Altona, *Ibid.*, **31**, 1337 (1976). (c) C. E. Blom, L. P. Otto, and C. Altona, *Ibid.*, **32**, 1137 (1976).

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(4) (a) W. B. Person, "Vibrational-Rotational Spectrometry for Planetary Atmospheres", Vol. I, M. J. Mumma, K. Fox, and J. Hornstein, Eds., NASA Conference Publication 2223, pp 89-123. (b) W. B. Person and J. D. Rogers, "Analytiktreffen", 1980 Schwingungs-Spektroskopie-Theorie und Anwendungen, pp 262-300.

(5) J. Overend, *Appl. Spectrosc.*, **37**, No. 1 (1983).

[†] On sabbatical leave (1983) from the Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02668 Warsaw, Poland.

the form in which they are found in nature. In order to understand the effects of intermolecular interactions on the spectrum of a molecule such as uracil, it is important first to understand the spectrum of the isolated molecule.

The quality of these predictions (factor of two) is such that they can be a considerable help in verifying experimental assignments of large (≥ 12 atoms) molecules. In fact, one of the most difficult problems in vibrational spectroscopy is an assignment of the fundamental modes for a molecule with 12 or more atoms and little symmetry. Assignments are usually made by use of the concept of characteristic group frequencies, by the vibration-rotation structure of gas-phase spectra, by comparison of Raman and infrared spectra with use of appropriate selection rules, by comparison of spectra of isotopically substituted molecules, by studies of polarized spectra of molecules in the crystalline phase, and by other spectroscopic tricks. However, molecules with 10–12 atoms or so are often not readily studied in the gas phase, and many of the other spectroscopic tricks also become more difficult to apply or to interpret with so many vibrational degrees of freedom. Hence, for molecules of this size it is often exceedingly difficult to make a unique vibrational assignment. This is true even in the case where theoretical predictions of the absorption frequencies are available. The large number of vibrational degrees of freedom and the general complexity of the spectrum still make it extremely difficult to assign it correctly. In such cases a reliable estimate (in this case even a "factor of two") of the infrared intensities can help greatly in reaching the correct assignment. For instance, if two fundamental modes are expected to be close in frequency, but one is expected to be very strong while the other is expected to be very weak, it will not usually be possible to decide on a correct assignment, based only on predicted frequencies. However, if the predicted intensities were also known (even within a "factor of two") the correct assignment of these two bands would probably be obvious. Uracil ($C_4H_4O_2N_2$) is a good example of a relatively large (12 atoms) molecule with a definitely complex spectrum that has not been unambiguously assigned, even with the available quantum mechanical predictions^{6–8} of the frequencies for its infrared spectrum.

At the same time, uracil is a typical example of a molecule that represents an extreme challenge to those who would attempt to calculate vibrational spectra. With its 12 atoms and 58 electrons, it is at the outer limit of the size that is currently feasible for ab initio calculations of its vibrational spectrum (both frequencies and intensities), particularly of its infrared spectrum.⁹ Uracil has $3N - 6 = 30$ vibrational modes, and its low symmetry (C_s) assures that all 30 modes are both infrared and Raman active and that there are no degenerate modes. It is this complexity that makes for the difficulty in assignment and which also makes it such a challenge for ab initio calculations. Finally, the importance of the uracil molecule as a nucleic acid constituent makes the thorough understanding of the vibrational spectrum of the isolated molecule doubly challenging.

There have been some previous attempts to make quantum mechanical calculations of the in-plane vibrational frequencies of uracil.^{6–8} Only one of these⁷ attempted to predict the intensities as well as the frequencies of the infrared absorption by the fundamental modes. The ab initio calculation by Nishimura, Tsuboi, Kato, and Morokuma⁶ was perhaps the most complete of these earlier studies, particularly in its comparison with earlier experimental work. Their ab initio calculations were with an STO-3G basis set to predict frequencies that could be scaled to predictions at the 4-31G level; the final predicted frequencies could be scaled again (by multiplying by a factor of 0.9) to agree quite

well with observed spectra.¹⁰ The CNDO/2 calculation by Csaszar and Harsanyi⁷ attempted also to predict the infrared intensities of all the modes for uracil. Both of these calculations were helpful, and both were used to reach an assignment of a new study of the infrared spectrum of the matrix isolated uracil molecule (and one of its deuterated derivatives) reported by Szczesniak et al.¹⁰

However, our previous experience with the prediction of vibrational intensities by CNDO/2 calculations¹¹ has led us to expect that they will not be very quantitative. Thus it is no surprise that the intensities calculated for uracil in the CNDO/2 calculation differ considerably from the experimentally observed relative intensities and are certainly not within the factor-of-two agreement that we would expect when ab initio techniques with a 4-31G basis set are used. Szczesniak et al.¹⁰ had tried to consider these intensities from the CNDO/2 calculation in assigning the spectrum of uracil, but it was obvious that the predicted intensities were not quantitatively correct. For instance, that calculation⁷ predicts the C–H stretching modes to be more intense than the N–H stretching modes. Experimentally, the latter are observed to be at least an order of magnitude greater in intensity than the C–H stretches. In addition, the observed spectrum¹⁰ in the 2000–1000-cm⁻¹ region is very complex, with many bands very close in energy to each other. The correct assignment of all of these bands is very difficult, even though the quantum mechanical predictions of the frequencies may be fairly accurate and the spectrum of the deuterated derivatives is known. We believe that quantum mechanical calculations of the infrared intensities for the parent molecule and its deuterated derivatives made using a 4-31G basis set are reliable enough to be of very considerable help in the assignment of this spectrum.

We have calculated the integrated infrared intensities for the in-plane vibrations of the uracil molecule and for seven of its deuterated derivatives by using ab initio methods, with a 4-31G basis set. The predicted intensities for the parent molecule, uracil, are in very good quantitative agreement with the experimentally observed relative intensities for the matrix isolated molecule. As expected, these predicted intensities for uracil and its deuterated derivatives are an extremely valuable tool in making the proper assignments for these complex molecules.

The atomic polar tensors (APTs) for the uracil molecule have also been calculated and are reported here. These tensors are expected to be valuable for the prediction of the intensities for other related bases as constituents of nucleic acids.

Calculations

The intensities were calculated with the GAUSSIAN 76 system¹² of ab initio programs with a 4-31G basis set.¹³ The integral threshold was set at 1.0×10^{-6} and the convergence limit at 5.0×10^{-5} , their standard values in the GAUSSIAN 76 program. The calculational procedure has been described fully elsewhere;^{1–4,14} suffice it to say here that the dipole derivatives were calculated by the method of finite differences, instead of by a gradient technique.^{15,16} The displacements of 0.01 Å were made in a mass-weighted Cartesian coordinate system as described previously.^{1a,3d} The density matrix obtained from the ab initio calculation of the wave function at the equilibrium configuration was used as the initial guess for that matrix in the calculations for the

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Table II. Calculated Wavenumbers ν and Absolute Intensities A for In-Plane Vibrations of N_1, N_3 -Dideuteriouracil Compared with the Experimental Frequencies and Relative Intensities for an Argon Matrix

| mode | assignment ^a | calcd values | | exptl values ^a | | |
|------------|--|-----------------------------|-------------------------------|-----------------------------|-------------------------------|-----|
| | | ν , cm ⁻¹ | A , km mol ⁻¹ | ν , cm ⁻¹ | rel intensity ^b | |
| ν_1 | N ₁ D str | 2556 | 58 | 2587 | 112 | |
| ν_2 | N ₃ D str | 2535 | 73 | 2549 | 73 | |
| ν_3 | C ₅ H str | 3070 | 10 | <i>c</i> | | |
| ν_4 | C ₆ H str | 3031 | 9 | <i>c</i> | | |
| ν_5 | C ₂ =O str | 1756 | 330 | 1767 | } <i>d</i> | 391 |
| | C ₅ =O str (in phase) | | | 1762 | | |
| | C ₅ =C ₆ str | | | 1750 | | |
| | | | | 1744 | | |
| | 1739 | | | | | |
| ν_6 | C ₄ =O str | 1750 | 1081 | 1713 | } <i>d</i> | 612 |
| | C ₂ =O str (out of phase) | | | 1703 | | |
| | C ₅ =C ₆ str | | | 1684 | | |
| ν_7 | C ₅ =C ₆ str | 1665 | 4 | 1634 | 9 | |
| | C ₂ =O str | | | | | |
| ν_8 | ring str | 1453 | 118 | 1440 | 164 | |
| ν_9 | ring str | 1104 | 8 | 1113 | 11 | |
| | C ₅ H bend | | | | | |
| | C ₆ H bend | | | | | |
| ν_{10} | C ₄ N ₃ str | 1388 | 101 | 1380 | 51 | |
| | C ₅ H bend | | | | | |
| | C ₆ H bend | | | | | |
| | ring str | | | | | |
| ν_{11} | C ₆ H bend | 900 | 6 | 915 | 22 | |
| | N ₁ D bend | | | | | |
| | C ₅ H bend | | | | | |
| ν_{12} | N ₁ D bend | 1325 | 17 | 1255 | 10 | |
| | N ₃ D bend | | | | | |
| | N ₃ D bend | | | | | |
| | N ₃ D bend | | | | | |
| ν_{13} | N ₃ D bend | 1289 | 82 | 1318 | 90 | |
| | C ₆ H bend | | | | | |
| | ring str | | | | | |
| ν_{14} | ring str | 1133 | 0.4 | <i>c</i> | | |
| ν_{15} | N ₁ D bend | 983 | 25 | 970 | 10 | |
| | C ₅ H bend, C ₆ H bend | | | | | |
| | N ₃ D bend | | | | | |
| ν_{16} | N ₃ D bend | 808 | 2 | 777 | 9 | |
| | N ₁ D bend | | | | | |
| | C ₆ H bend, C ₅ H bend | | | | | |
| ν_{17} | ring breath | 734 | 5 | 724 | 7 | |
| ν_{18} | ring def | 552 | 11 | 543 | 7 | |
| ν_{19} | C ₂ O bend, C ₄ =O bend | 531 | 9 | 524 | 7 | |
| | N ₁ D bend, N ₃ D bend | | | | | |
| ν_{20} | C ₂ =O bend | 491 | 25 | 508 | 28 | |
| | C ₄ =O bend, N ₃ D bend | | | | | |
| ν_{21} | C ₂ =O bend, C ₄ =O bend | 370 | 26 | 388 | 19 | |

^a From ref 10. See Table I footnote. ^b These integrated intensities are relative to ν_2 having an intensity of 73 units for this molecule also. ^c Not observed experimentally. ^d These bands are due to the fundamental modes expected here in Fermi resonance with one or more combination bands (see ref 10).

oratory. The assignments of the vibrations given in Tables I and II are made by observing the actual motions involved in each vibration rather than by an analysis of the potential energy distributions (PEDs).⁶

Tables III and IV give the predicted wavenumbers and intensities for all 21 in-plane fundamental modes for the remaining six deuterated derivatives of uracil. We expect these predicted values to be helpful in assigning the spectra of the isolated deuterated molecules. For example, the experimental spectra of the N_1, N_3 -dideuterated molecule isolated in argon matrices reported previously¹⁰ agrees very well with the predicted values given in Table II, as indicated there.

So far, experimental values for the absolute intensities of the fundamental vibrations of the isolated uracil molecule have been reported only for N_1H and N_3H stretching vibrations of 3-methyluracil and 1-methyluracil in gas-phase studies.¹⁹ These

intensities were found to be 75 and 53 km mol⁻¹ for N_1H and N_3H stretching modes, respectively. The value for the intensity of the N_1H mode agrees very well with the predicted intensity for this mode in uracil (70 km mol⁻¹). The experimental intensity of the N_3H stretching vibration in 1-methyluracil is lower (53 km mol⁻¹) than the predicted value (98 km mol⁻¹), but it is within the limit of the expected "factor of two".

We have recently measured also the total intensity of ν_5 and ν_6 in the carbonyl region for 1-methyluracil in CDCl₃ solution and 1,3-dimethyluracil in CDCl₃ and CCl₄ solutions. For 1-methyluracil in CDCl₃, the measured intensity in this region is 1464 km mol⁻¹; for 1,3-dimethyluracil in CDCl₂ it is 1220 km mol⁻¹; and in CCl₄ solution it is 1100 km mol⁻¹. All these values are very close to the total predicted value of 1466 km mol⁻¹ for ν_5 and ν_6 of uracil.

It should be mentioned that our calculation of intensities for normal modes of methylated uracils with use of the same procedures as described here for uracil predicts values for the intensities of the N_1H and N_3H stretches and for the total carbonyl

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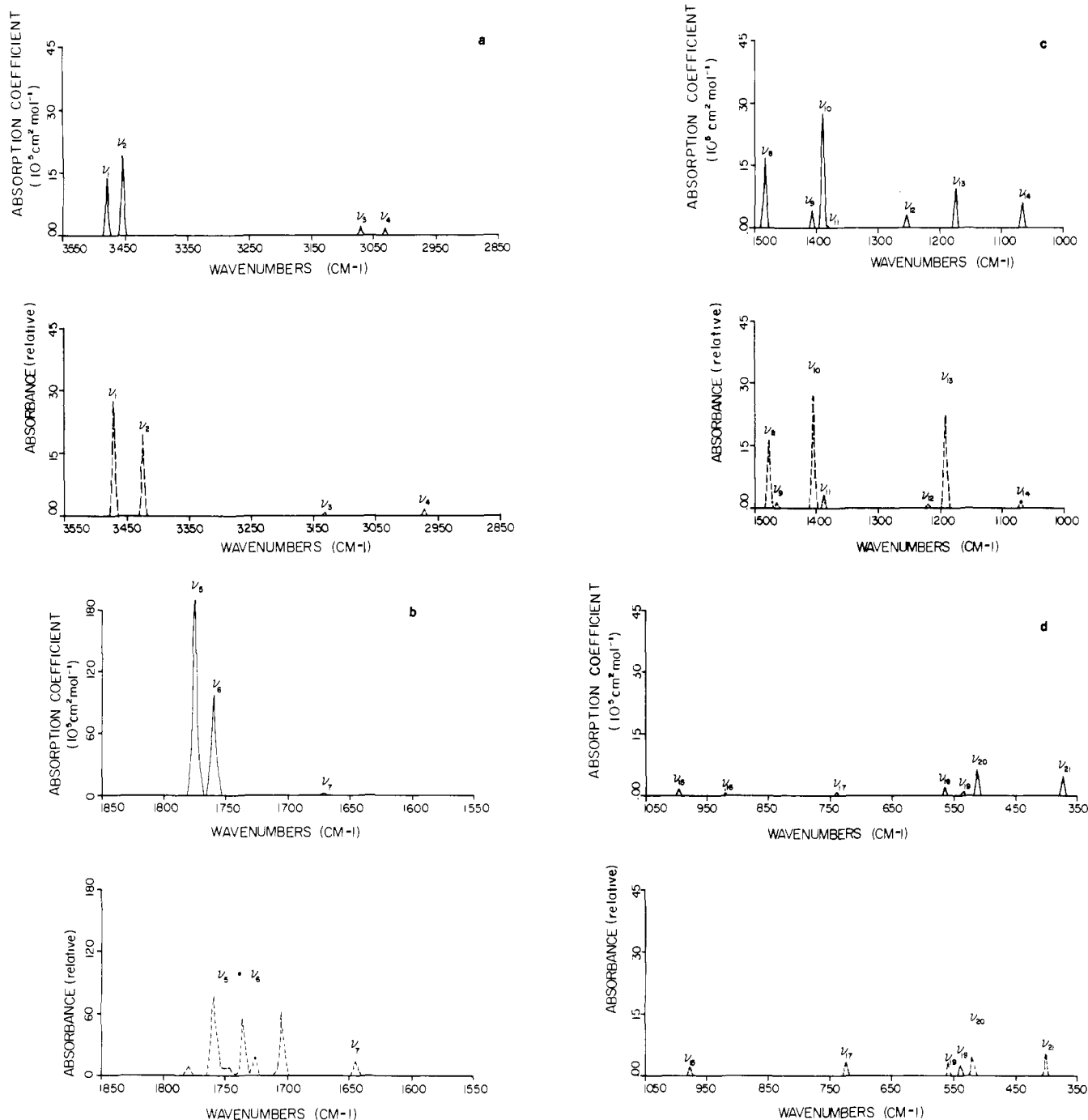


Figure 2. Comparison of the calculated (—) and experimental (---) spectra for the 21 fundamental in-plane vibrational modes of uracil. The half-width for all bands is kept constant at 5 cm^{-1} , estimated from the matrix spectrum. Intensity scales correspond to the integrated intensities from Tables I and II, divided by the half-width (5 cm^{-1}). The assignment corresponds to that given in Table I. (a) The C—H and N—H stretching region. (b) The C=O and C=C stretching region. (c) The ring stretching, ring bending, and N—H and C—H bending region. (d) The ring breathing, ring deformation, and C=O bending region.

stretching region that are practically unchanged from the intensities for the corresponding modes of uracil.²⁰

All the calculated intensities for uracil are compared in Table I with the relative integrated experimental intensities supplied by Szczesniak et al.¹⁰

We believe the calibration of this relative intensity scale by the measurements of absolute intensities reported above suggests that the relative values¹⁰ in Table I are quite close to the absolute intensities (within $\pm 20\%$ or so). A simulated spectrum of uracil from the calculated values of scaled wavenumbers and absolute intensities is compared in Figure 2 with the experimental spectrum

of uracil isolated in a nitrogen matrix. For the simulation, all bands were assumed to have the same constant half-width (5 cm^{-1} , estimated from the observed matrix spectrum) to allow a reliable visual comparison between peak heights in Figure 2 for the calculated and experimental spectra.

We can see from Figure 2 that the predicted intensity pattern agrees closely with the experimental spectrum. The intensity by ν_7 is calculated to be relatively low, although it is found to be quite strong in the experimental spectrum. However, the relative intensities predicted for the remaining 20 in-plane modes are seen to be in surprisingly good agreement with experiment. The only exception found in the original prepublication assignment by Szczesniak et al.¹⁰ was ν_{13} and ν_{14} . Their original unpublished assignment had placed ν_{14} at higher frequency (1192 cm^{-1}) and

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Table III. Calculated Wavenumbers ν and Absolute Intensities A for In-Plane Vibrations of N_1 -Deuteriouracil and N_3 -Deuteriouracil

| mode ^a | N_1 -deuteriouracil | | N_3 -deuteriouracil | |
|-------------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------|
| | ν , cm ⁻¹ | A , km mol ⁻¹ | ν , cm ⁻¹ | A , km mol ⁻¹ |
| ν_1 | 2558 | 59 | 3479 | 69 |
| ν_2 | 3454 | 98 | 2535 | 71 |
| ν_3 | 3070 | 10 | 3070 | 10 |
| ν_4 | 3031 | 9 | 3031 | 9 |
| ν_5 | 1767 | 1087 | 1766 | 435 |
| ν_6 | 1757 | 333 | 1752 | 1024 |
| ν_7 | 1666 | 2.7 | 1669 | 3 |
| ν_8 | 1455 | 124 | 1482 | 86 |
| ν_9 | 1402 | 44 | 1106 | 9 |
| ν_{10} | 1383 | 62 | 1381 | 126 |
| ν_{11} | 887 | 4 | 1393 | 40 |
| ν_{12} | 1247 | 46 | 1325 | 16 |
| ν_{13} | 1296 | 59 | 1184 | 30 |
| ν_{14} | 1127 | 2 | 1066 | 29 |
| ν_{15} | 991 | 26 | 984 | 7 |
| ν_{16} | 936 | 4 | 821 | 2 |
| ν_{17} | 738 | 5 | 735 | 6 |
| ν_{18} | 558 | 12 | 562 | 9 |
| ν_{19} | 528 | 5 | 532 | 10 |
| ν_{20} | 507 | 29 | 500 | 26 |
| ν_{21} | 373 | 27 | 372 | 25 |

^aSee Table I for approximate mode description. Some change in description from uracil is expected because of the changes in mass on deuteration.

higher intensity than ν_{13} (1070 cm⁻¹). Our calculations indicate that ν_{13} should be both at higher frequency and of higher intensity than ν_{14} . After our predictions became available, Szczesniak et al. modified their assignment to agree with the predictions here. Aside from this, the calculated integrated intensities confirmed the original assignment of the in-plane modes given by Szczesniak and co-workers.

Similar comments can be made about the comparison between the calculated and experimental wavenumbers and intensities for N_1, N_3 -dideuterated uracil given in Table II and shown as a simulated spectrum in Figure 3. The agreement here is also very good. The intensities for several of the bands are predicted to

be lower than those observed experimentally (i.e., ν_7, ν_8, ν_9 , and ν_{16}), but nevertheless the overall agreement is well within the typical "factor of two" one would normally expect for these calculations. Here also a discrepancy existed between the original unpublished assignment of Szczesniak et al.¹⁰ and our calculated values. In addition, there was considerable uncertainty in the assignment of ν_9, ν_{11} , and ν_{15} . Szczesniak et al.¹⁰ had originally assigned ν_{14} to the high-intensity band at 1318 cm⁻¹, and ν_{13} as too weak to be observed experimentally. We calculate ν_{13} to be relatively strong while ν_{14} is predicted to be very weak (0.04 km mol⁻¹). Hence, the band not observed experimentally must be ν_{14} and the original assignment of ν_{13} and ν_{14} again was interchanged.¹⁰ The assignment of the ν_9, ν_{11} , and ν_{15} modes in N_1, N_3 -dideuterated uracil are also not obvious from the experimental spectrum. In the original assignment, two possible assignments were considered for all three cases. The predicted intensities agreed with only one assignment in preference to the other. On the basis of the predicted intensities ν_9 should be assigned at 1113 cm⁻¹ (as opposed to 1450 cm⁻¹), ν_{11} at 915 cm⁻¹ (vs. 970 cm⁻¹ originally), and ν_{15} at 970 cm⁻¹ (as opposed to 915 cm⁻¹), and the original assignment was changed accordingly in the published paper.¹⁰

One final comment on the predicted and experimental spectrum of N_1, N_3 -dideuterated uracil should be discussed here. In uracil, the predicted rates of intensities for $\nu_5(C_2=O)/\nu_6(C_4=O)$ is 1.64. Experimentally, an exact ratio of the relative intensities cannot be determined because of the complexity of the spectrum in this region due to Fermi resonance, but reasonable assignments of the latter give a ratio in reasonable agreement with the calculation. In the N_1, N_3 -dideuterated species, this predicted ratio is 0.30 in good qualitative agreement with the experimental spectrum for the dideuterated species. This indicates that the puzzling reversal of the ratio (from 1.96 in uracil to 1/2.98 in N_1, N_3 -dideuterated uracil) of the intensities for these two bands observed in the experimental spectrum is possibly not only due to Fermi resonance but is also a result of the changing normal coordinates upon deuteration. To us, this result is one of the most satisfying examples of the utility of "factor-of-two" intensity calculations as an aid to understanding a complex experimental spectrum.

It should be emphasized that we do not expect the calculated values of the absolute intensities to be more accurate than the "factor of two" discussed elsewhere. Ab initio quantum mechanical calculations can indeed be made that are much more reliable (see

Table IV. Calculated Wavenumbers ν and Absolute Intensities A for In-Plane Vibrations of C_3 -Deuteriouracil, C_6 -Deuteriouracil, C_3, C_6 -Dideuteriouracil, and Perdeuteriouracil

| mode ^a | C_3 -deuteriouracil | | C_6 -deuteriouracil | | C_3, C_6 -deuteriouracil | | perdeuteriouracil | |
|-------------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|-------------------------------|
| | ν , cm ⁻¹ | A , km mol ⁻¹ | ν , cm ⁻¹ | A , km mol ⁻¹ | ν , cm ⁻¹ | A , km mol ⁻¹ | ν , cm ⁻¹ | A , km mol ⁻¹ |
| 1 | 3479 | 68 | 3479 | 70 | 3479 | 68 | 2557 | 56 |
| 2 | 3454 | 98 | 3454 | 98 | 3454 | 98 | 2535 | 72 |
| 3 | 2282 | 14 | 3068 | 11 | 2289 | 12 | 2289 | 11 |
| 4 | 3033 | 8 | 2258 | 16 | 2250 | 18 | 2249 | 16 |
| 5 | 1774 | 877 | 1774 | 896 | 1774 | 872 | 1755 | 479 |
| 6 | 1753 | 587 | 1757 | 562 | 1751 | 79 | 1742 | 932 |
| 7 | 1659 | 12 | 1647 | 18 | 1634 | 33 | 1628 | 20 |
| 8 | 1474 | 105 | 1471 | 98 | 1463 | 110 | 1428 | 184 |
| 9 | 1402 | 6 | 1402 | 10 | 1401 | 6 | 1279 | 55 |
| 10 | 1384 | 117 | 1004 | 10 | 1016 | 26 | 1032 | 10 |
| 11 | 1355 | 16 | 1329 | 15 | 1300 | 22 | 859 | 13 |
| 12 | 991 | 18 | 1252 | 13 | 987 | 17 | 968 | 19 |
| 13 | 1131 | 47 | 1389 | 147 | 1382 | 120 | 1355 | 42 |
| 14 | 1229 | 35 | 1063 | 33 | 1181 | 22 | 1186 | 3 |
| 15 | 942 | 1 | 984 | 11 | 851 | 1 | 817 | 0.58 |
| 16 | 842 | 0.1 | 842 | 5 | 822 | 4 | 779 | 0.3 |
| 17 | 736 | 6 | 727 | 4.7 | 725 | 6 | 718 | 6 |
| 18 | 563 | 10 | 561 | 11 | 559 | 10 | 549 | 10 |
| 19 | 519 | 9 | 530 | 9 | 517 | 14 | 512 | 14 |
| 20 | 507 | 28 | 509 | 27 | 503 | 22 | 487 | 18 |
| 21 | 373 | 26 | 374 | 25 | 372 | 25 | 370 | 26 |

^aSee Table I for approximate mode description. Some change in description from uracil are expected because of the changes in mass on deuteration.

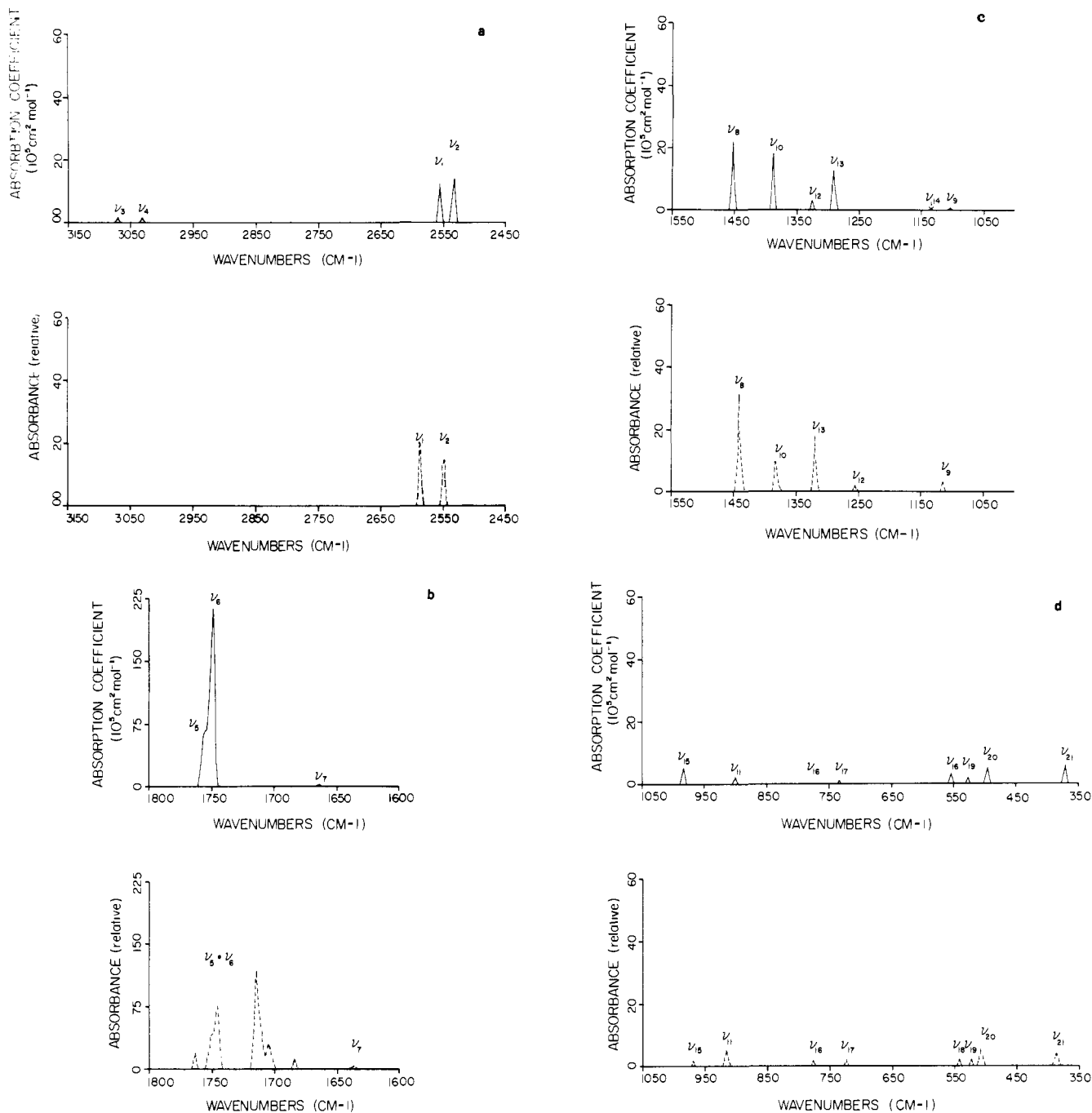


Figure 3. Comparison of the calculated (—) and experimental (---) spectrum for the 21 fundamental in-plane vibrational modes of N_1N_3 -dideuterated uracil. The half-width for all bands is kept constant at 5 cm^{-1} , estimated from the matrix spectrum. Intensity scales correspond to the integrated intensities from Tables I and II, divided by the half-width (15 cm^{-1}). The assignment corresponds to that given in Table II. (a) The C—H and N—D stretching region. (b) The C=O and C=C stretching region. (c) The ring stretching, ring bending, and C—H bending region. (d) The ring breathing, ring deformation, C=O bending, and N—D bending region.

ref 1, 4, 9, 15, 16, and 22 for more discussion). In fact, however, it is not entirely clear when we examine Tables I and II whether the differences between calculated and experimental intensities are due to errors in the former or uncertainties in the latter. Nevertheless, we can be quite certain that the intensity predicted for ν_7 is too low. Perhaps a few other examples (maybe ν_{16} ?) also indicate errors still remaining in the calculation, but on the whole the nearly quantitative overall agreement (within both uncertainties) between both the scaled calculated frequencies and the calculated intensities with the observed values is astonishingly good considering the possible errors in both the calculations and the experiment.

The calculated results for the remaining six deuterated derivatives of uracil are given in Tables III and IV. The assignments of the normal modes in these tables were based on the character

of the parent vibrational modes given for uracil in Table I (and therefore on the expected shifts with specific deuterated sites) and the assumption that the intensity of any single band should not change drastically upon deuteration. Values of PEDs for deuterated uracils are given elsewhere.²² We believe that these predictions in Tables III and IV are quite reliable, based on the very good quantitative agreement found between the predicted and experimental frequencies and intensities for uracil and for its N_1, N_3 -dideuterated homologue. We have recently learned of new experimental studies of the spectra of some of these matrix

(21) A. J. Barnes, M. A. Stuckey, and L. LeGall, *Spectrochim. Acta*, to be published.

(22) K. Szczepaniak, M. Szczesniak, M. J. Nowak, I. Scott, S. Chin, and W. B. Person, *Int. J. Quantum Chem.*, submitted for publication.

Table V. Calculated Atomic Polar Tensors (APTs)^a for Uracil in the Principal Cartesian Coordinate System of Figure 1^b

| | |
|---|--|
| $P_x(N_1) = \begin{pmatrix} -0.957 & 0.163 & 0 \\ -0.678 & -0.978 & 0 \\ 0 & 0 & -0.729 \end{pmatrix}$ | $P_x(C_2) = \begin{pmatrix} 1.641 & 0.238 & 0 \\ 0.443 & 1.988 & 0 \\ 0 & 0 & 0.850 \end{pmatrix}$ |
| $P_x(N_3) = \begin{pmatrix} -0.623 & -0.054 & 0 \\ -0.094 & -1.403 & 0 \\ 0 & 0 & -0.660 \end{pmatrix}$ | $P_x(C_4) = \begin{pmatrix} 1.449 & 0.014 & 0 \\ -0.677 & 1.557 & 0 \\ 0 & 0 & 0.680 \end{pmatrix}$ |
| $P_x(C_5) = \begin{pmatrix} -0.549 & 0.110 & 0 \\ 0.565 & -0.444 & 0 \\ 0 & 0 & -0.428 \end{pmatrix}$ | $P_x(C_6) = \begin{pmatrix} 0.437 & -0.244 & 0 \\ 0.372 & 1.254 & 0 \\ 0 & 0 & 0.268 \end{pmatrix}$ |
| $P_x(H_7) = \begin{pmatrix} 0.191 & 0.076 & 0 \\ -0.029 & 0.236 & 0 \\ 0 & 0 & 0.437 \end{pmatrix}$ | $P_x(O_8) = \begin{pmatrix} -0.942 & -0.552 & 0 \\ -0.482 & -1.232 & 0 \\ 0 & 0 & -0.619 \end{pmatrix}$ |
| $P_x(H_9) = \begin{pmatrix} 0.275 & -0.005 & 0 \\ -0.058 & 1.158 & 0 \\ 0 & 0 & 0.446 \end{pmatrix}$ | $P_x(O_{10}) = \begin{pmatrix} -0.908 & 0.251 & 0 \\ 0.620 & -1.309 & 0 \\ 0 & 0 & -0.592 \end{pmatrix}$ |
| $P_x(H_{11}) = \begin{pmatrix} 0.027 & -0.022 & 0 \\ 0.005 & 0.114 & 0 \\ 0 & 0 & 0.197 \end{pmatrix}$ | $P_x(H_{12}) = \begin{pmatrix} -0.041 & 0.023 & 0 \\ 0.013 & 0.060 & 0 \\ 0 & 0 & 0.151 \end{pmatrix}$ |

^aAPTs as defined in ref 23. ^bUnits are e; $1 e = 1.602 \times 10^{-19} C$. (Numbering of atoms is as given in Figure 1.) These values have been calculated as indicated in the text for displacements of all atoms. Their reliability can be tested by checking to see that the null condition $\sum P^a = 0$ holds true. For information, the calculated value of the dipole moment in our equilibrium configuration is $1.15 e \text{ \AA}$ ($1 e \text{ \AA} = 4.80 D$), compared to 0.833, experimentally (M. Geller, A. Pohorille, and A. Jaworski, *Biochim. Biophys. Acta*, 331 (1973)).

isolated species,²¹ and we expect that comparison of these experimental results with the calculated values in Tables II-IV will be of considerable interest.

The atomic polar tensors (APTs)²³⁻²⁵ for all 12 atoms of uracil are given in Table V for the coordinate system shown in Figure 1. These similarities and differences between these APTs and those for the same atoms in similar chemical environments of other molecules will be discussed and analyzed elsewhere, as will the possibility for the reliable prediction of infrared intensities in other nucleic acid constituents by transferring these APTs. For the present, the main value of the APTs listed in Table V is just that these are the parameters that we have calculated here for uracil, and the absolute intensities given in the other tables are obtained from these values.

Conclusions

The infrared spectra of large biologically important molecules are very complicated. Due to the extreme complexity of these spectra and the difficulty even to observe the spectrum of the isolated molecules, complete assignments have in general not been made solely on the basis of spectroscopic evidence, even including the spectra of deuterated species. For such cases it is extremely useful to have quantum mechanical predictions of the infrared spectrum, including integrated intensities, as well as the predictions for normal coordinates and absorption frequencies. Of course, it is desirable for such predictions to be as reliable as possible, but "factor-of-two" intensity predictions and scaled frequencies can be very helpful, indeed.

(23) J. F. Biarge, J. Herranz, and J. Morcillo, *An. R. Soc. Esp. Fis. Quim. Ser. A*, **57**, 81 (1961).

(24) (a) W. B. Person and J. H. Newton, *J. Chem. Phys.*, **61**, 1040 (1974).
(b) J. H. Newton and W. B. Person, *ibid.*, **64**, 3036 (1976).

(25) W. B. Person, in "Vibrational Intensities in Infrared and Raman Spectroscopy"; W. B. Person and G. Zerbi, Eds., Elsevier, Amsterdam, 1982, Chapters 4 and 14.

We have shown that ab initio calculations with a 4-31G basis set can be used for such predictions of the integrated intensities of molecules as large and complex as uracil. For uracil the assignment has been worked on for a number of years (for example, see references given in ref 6 and 10) so it has been possible to check that the calculated spectrum agrees quite well with the experimental spectrum for the isolated molecule. We can therefore believe that the slight modifications in the assignment for that molecule that are suggested by comparison of the calculated spectrum with the experimental spectrum are indeed justified. Furthermore, we can have considerable confidence in similar predictions for similar molecules.

As can be seen, our viewpoint on the usefulness of predicted spectra and our judgment of how well predictions and experiment agree is somewhat different than that of the theoretician. In a previous calculation of frequencies and intensities for a molecule (benzene) of this size,⁹ the authors were primarily concerned with trying to obtain complete quantitative agreement between calculated values and experiment. To us, as experimentalists trying to assign and interpret spectra, the calculations even in this limited form are quantitative enough to be very useful. We hope this example has illustrated this usefulness.

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Registry No. Uracil, 66-22-8; uracil-*N*₁,*N*₃-*d*₂, 20666-60-8; uracil-*C*₅,*C*₆-*d*₂, 24897-52-7; uracil-*N*₁,*N*₃,*C*₅,*C*₆-*d*₄, 24897-55-0; uracil-*C*₅-*d*, 24897-50-5; uracil-*C*₆-*d*, 24897-51-6; uracil-*N*₁-*d*, 89890-33-5; uracil-*N*₃-*d*, 90063-28-8.