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Registry No. H_2, 1333-74-0; $CH_3^{\bullet}$, 2229-07-4; $C_2H_5^{\bullet}$, 2025-56-1; *i*-$C_3H_7^{\bullet}$, 2025-55-0; HBr, 10035-10-6; D_2, 7782-39-0; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; Br, 10097-32-2; I_2, 7553-56-2; *t*-$C_4H_9^{\bullet}$, 1605-73-8; acetone, 67-64-1; acetone-d_6, 666-52-4; diethyl ketone, 96-22-0; diisopropyl ketone, 565-80-0.

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2 + 1 REMPI Spectra of Cyclic Ketones in a Cold Molecular Beam. 2. The n → 3s Rydberg Transition of Methyl-Substituted Cyclohexanones and Cyclopentanones

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Abstract: The two-photon excitation of the n → 3s Rydberg transition in monomethyl and dimethyl isomers of cyclohexanone and cyclopentanone has been studied by resonance enhanced multiphoton ionization (2 + 1 REMPI). This transition has been found to be highly sensitive to both the orientation and position of methyl substituents on the cyclic ketone ring. Cis and trans configurations of dimethyl isomers show characteristic 3s transition energy shifts which are additive in nature and can be used to predict the transition energy of other structures. The spectroscopic energies of configurational isomers appear to reflect relative ground-state stabilities. This correlation has been supported by thermodynamic data and molecular mechanics calculations of ground-state energies. Laser polarization effects are found to be useful in determining the degree of chromophore asymmetry in chiral molecules.

I. Introduction

Recent advances in laser and molecular beam technology have enabled the high resolution examination of ultraviolet transitions in large molecules. In the past, solution phase electronic absorption has been of limited value for structural analysis due mainly to broad absorption bands and complicated spectral congestion. However, numerous recent studies of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of aromatics and heterocycles in cold molecular beams have shown the electronic spectrum to be highly sensitive to structure and location of alkyl substituents at various ring positions.[1,2a] The present study shows that the n → 3s transition of saturated cyclic ketones is particularly sensitive to molecular configuration. In fact, the relative shifts of the 3s transition energies in methyl-substituted cyclic ketones can be correlated with the ^{13}C NMR chemical shifts of the carbonyl carbons in the same series of isomers. This relationship will be discussed in a future publication.[3]

Since hot ro-vibrational transitions are greatly reduced in cold molecular beam spectroscopy, the severe spectral congestion normally observed in electronic spectra is dramatically simplified. If the transitions are chosen so that little nuclear reorientation occurs in the excited state (such as in the promotion of a nonbonding electron to nonbonding orbitals), the resulting vibrational spectrum is rather uncomplicated compared to the ground-state IR spectrum since only those frequencies which change upon excitation are observed. Once identified, these vibrational modes aid in determing both ground- and excited-state molecular structure.

The electronic levels observed in resonance enhanced multiphoton ionization (REMPI) are predominantly long-lived Rydberg orbitals. These states, located in the far and vacuum UV spectral regions, are often obscured by overlapping valence transitions in conventional one-photon absorption. Since the REMPI signal is dependent upon long lifetimes of the intermediate state, valence levels are normally suppressed in the MPI spectrum[4] due to the dissociative nature of antibonding orbitals. The atomic-like Rydberg states have received less attention than the lower energy valence shell orbitals so that little is known about their sensitivity to molecular structure compared to the shifts observed in chromophores absorbing in the near UV and visible spectral regions.

We have investigated the REMPI spectrum of cyclic ketones through the intermediate 3s Rydberg state for the purpose of studying the transition's sensitivity to stereochemistry. The Rydberg spectrum is generated by scanning a dye laser across an easily accessible wavelength region (380–420 nm) producing the desired resonance ionization through a two-photon absorption to the 3s state. In a previous study,[5] this transition was examined in unsubstituted cyclic ketones of various ring sizes. The samples were seeded in a cold molecular beam and ionized by using a 2 + 1 REMPI scheme. Briefly, the results included the following points. The promotion of the nonbonding electron to the 3s Rydberg state was found to have a significant effect on the carbonyl geometry. The C═O stretching frequency was reduced from about 1730 cm^{-1} in the ground state to approximately 1250 cm^{-1} in the 3s state, a decrease that is consistent with an increased C═O bond length in the excited state. In addition, the electronic transition is accompanied by the excitation of low-frequency ring bending and torsional modes which appear to be a consequence of sp^2 hybridization relaxation in the excited state and subsequent reorientation to a less strained geometry. The shift in the 3s transition origin was found to correlate with the C–CO–C bond angle, reflecting the release of angle strain. Laser polarization effects characteristic of two-photon transitions were used to aid in the identification of some excited state vibrational modes. In this study, we have examined the n → 3s transition of methyl-substituted isomers of cyclohexanone and cyclopentanone. The array of spectroscopic parameters studied includes the shift in the

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(1) Sin, C. H.; Tembreull, R.; Lubman, D. M. *Anal. Chem.* **1984**, *56*, 2776. Tembreull, R.; Sin, C. H.; Li, P.; Pang, H. M.; Lubman, D. M. *Anal. Chem.* **1985**, *57*, 1186. Tembreull, R.; Sin, C. H.; Pang, H. M.; Lubman, D. M. *Anal. Chem.* **1985**, *57*, 2911.

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Table I. Transition Origins, Relative Shifts, and Ω^a Values for Methyl Isomers of Cyclohexanone and Cyclopentanone

	n→3s origin (cm^{-1})	rel shift	Ω
(1) cyclohexanone	50717	0	1.5
(2) 4-methylcyclohexanone	50710	−7	1.5
(3) 3-methylcyclohexanone	50862	+145	1.5
(4) *trans*-3,5-dimethylcyclohexanone	50464	−253	0.9
(5) *cis*-3,5-dimethylcyclohexanone	50955	+238	1.5
(6) *cis*-3,4-dimethylcyclohexanone	50321	−396	1.3
(7) *trans*-3,4-dimethylcyclohexanone	50853	+136	1.5
(8) 2-methylcyclohexanone	50171	−546	0.6
(9) 2-ethylcyclohexanone	50103	−614	1.0
(10) *trans*-2,5-dimethylcyclohexanone	50327	−390	0.7
(11) *cis*-2,5-dimethylcyclohexanone	49750	−967	1.5
(12) *cis*-2,6-dimethylcyclohexanone	49756	−961	1.5
(13) *trans*-2,6-dimethylcyclohexanone	49446	−1271	1.5
(14) cyclopentanone	50068	0	1.5
(15) 3-methylcyclopentanone	50308	+240	0.9
(16) *cis*-3,4-dimethylcyclopentanone	50079	+11	0.7
(17) *trans*-3,4-dimethylcyclopentanone	50523	+455	1.5
(18) 2-methylcyclopentanone	49691	−377	0.8
(19) *trans*-2,4-dimethylcyclopentanone	49801	−267	0.6
(20) *cis*-2,4-dimethylcyclopentanone	49956	−112	0.7

[a] $\Omega = I_{cir}/I_{lin}$.

n → 3s transition energy, vibrational fine structure of the excited state, relative intensities of the vibrational bands, and laser polarization effects which govern multiphoton ionization rates.

II. Experimental Section

The molecular beam apparatus is the same as described in the previous paper.[5] The resonance enhanced MPI data were produced with a Lumonics excimer pumped dye laser held at constant intensity (about 500 μJ/pulse) with a microprocessor controlled feedback loop coupled to a calorimeter. Laser polarization was accomplished in three stages. A calcite prism was used to produce pure plane polarized light, followed by a half-wave plate consisting of two Fresnel rhombs used to rotate the plane of polarization. Finally, a single rhomb was used to alternate between circular and linear polarization. The laser beam was focussed with a 5-cm diameter fused silica lens (focal length: 25 cm), producing a medium-tight focal cross-section.

The molecular beam was produced with a Laser Technics 203 pulsed valve. All samples were purchased either from Aldrich Chemical, Wiley Organic, Columbia Organic, or Pfaltz and Bauer. The only sample purified was a cis/trans mixture of 3,5-dimethylcyclohexanone which was separated into its component epimers on a 20% SF-96 GC column. Samples were introduced by first freezing them in liquid N_2 and then allowing the liquid to evaporate at room temperature into the inlet system filled with 10–50 Torr of argon. After equilibration, 300 Torr of argon was backfilled into the system producing a seeded beam of approximately 1–5%. The beam was skimmed 3 cm downstream from the 0.3-mm nozzle and intersected the laser beam 4 cm beyond the skimmer.

For the experiments reported here, only the total ionization signal was desired. This was accomplished by acceleration of the electrons in a high draw-out field of 1000 V/cm and detection with a chevron microchannel plate. The high draw-out field insured a high collection efficiency yet did not interfere with the excitation process to the low-lying 3s Rydberg state. A Stanford Research SR250 gated integrator was used to collect the signal pulse followed by digital conversion and processing by using a Stanford Research SR245 computer interface coupled to an IBM PC. The laser was smoothly scanned, while the computer recorded the signal in a strip-chart fashion.

III. Results

The n → 3s 2 + 1 REMPI spectra of various mono- and dimethylcyclohexanone isomers substituted at the C3, C4, and C5 ring positions are shown in Figure 1. Each spectrum has a dominant origin peak (Table I) with relatively little excitation in the vibrational modes. Compared to unsubstituted cyclohexanone **1**, three of the isomers have transition origins shifted to higher energy while two are shifted to lower energy. The 3,4 and 3,5-dimethyl structures exist as either cis or trans configurations, each displaying a distinctive transition energy.

The n → 3s transition of cyclohexanone isomers with at least one group substituted at the α-carbon position are plotted in Figure 2. In these spectra, each transition is significantly red shifted compared to unsubstituted cyclohexane and shows a high degree of excitation in the lowest energy vibrational mode. The 2,5- and 2,6-dimethyl structures can also exist as either cis or trans configurations clearly distinguishable by the energy of their 3s transition. This demonstrates that the n → 3s origin is sensitive

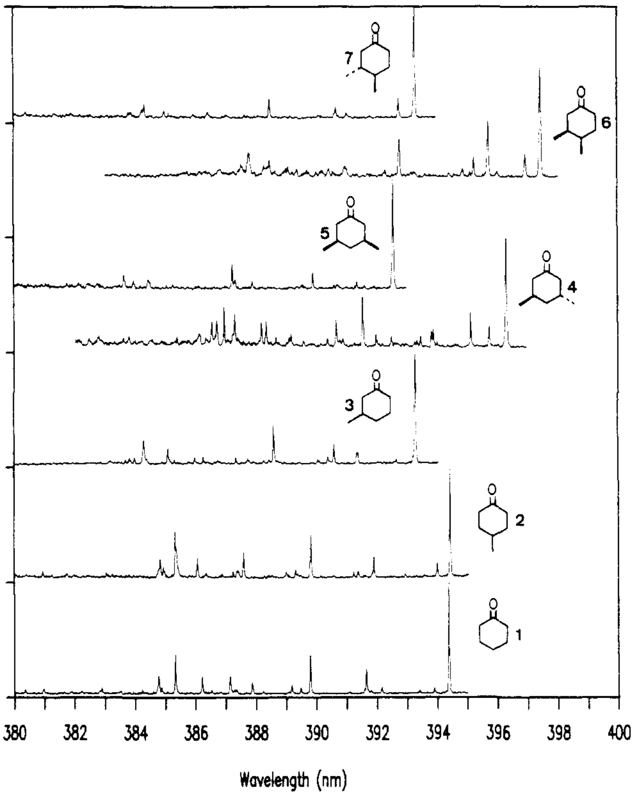

Figure 1. The two-photon n → 3s transition of cyclohexanone methyl isomers substituted at C3, C4, and C5 positions.

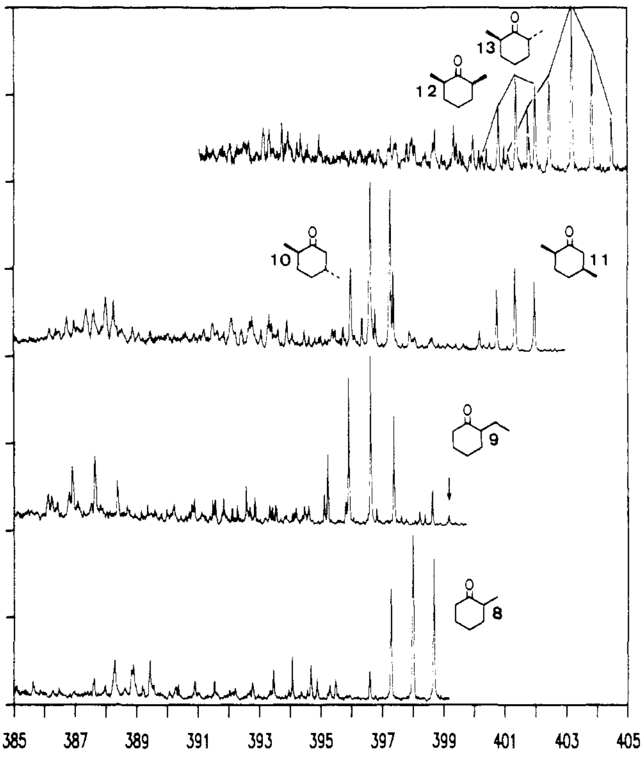

Figure 2. The two-photon n → 3s transition of cyclohexanone methyl isomers with at least one group substituted at the C2 position. The arrow in the spectrum of structure **9** indicates the transition origin.

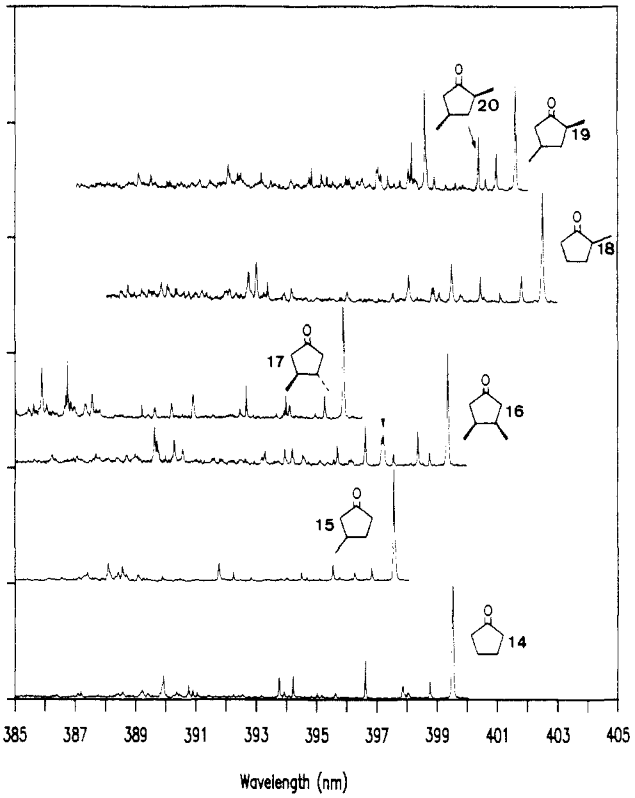

Figure 3. The two-photon n → 3s transition of cyclopentanone methyl isomers.

not only to the location of methyl substitution but also to the orientation of each methyl group.

The 3s spectra of methyl-substituted cyclopentanones are plotted in Figure 3. Each displays a dominant origin peak whose transition energy follows the same patterns observed in those isomers of Figures 1 and 2. That is, compared to unsubstituted cyclopentanone, the 3-methyl isomer is blue shifted, exhibiting less vibrational excitation; the 2-methyl isomer is red shifted with a higher degree of low frequency vibrational intensity. As in the case of cyclohexanone, the spectra of cis and trans configurations of dimethyl substitution at C3 and C4 are unique to each structure.

One of the most interesting features of the spectra in Figures 1–3 is the alternating nature of the shift in the n → 3s transition energy. Note, for instance, that a single methyl substitution on cyclohexanone at C3 (**3**) blue shifts the origin by 145 cm^{-1}. A second methyl group substituted at the symmetrically equivalent C5 position further shifts the origin by either 93 cm^{-1} to the blue (**5**) or 398 cm^{-1} to the red (**4**). These shifts are of interest because the electronic transitions of methyl-substituted heterocyclic ring systems, such as the $\pi \rightarrow \pi^*$ transition of methyl indoles[2a] and the n → 3s transition of picolines,[2b] are characterized only by red shifts relative to the unsubstituted molecule. Such spectroscopic shifts are attributed to a reduction of the excited-state energy due to the alkyl substitution. However, in the cyclic ketone system, a methyl group substituted at the same ring position but in different orientations relative to the ring plane causes the 3s transition energies to shift in opposite directions.

In the Discussion section, the additivity of these spectral shifts and its application to structural analysis will be examined. This is followed by a comparison of the n → 3s energy shifts to the respective ground-state conformational stabilities. Finally, the influence of laser polarization on the MPI signal intensity of chiral molecules will be discussed.

A. Cyclohexanone Methyl Isomers. The connection between changes in molecular structure upon excitation and the spectra in Figures 1–3 is based on the Franck–Condon principle. An unstrained molecule in the ground electronic state is expected to retain its geometry in the excited state if a nonbonding electron is promoted to a nonbonding orbital such as the n → 3s excitation of a ketone. This transition would be highly vertical, resulting in very little excitation of any vibrational modes. In contrast, a molecule which is capable of reorientation to a more stable conformation in the excited state will display vibrational excitation localized to the modes which are affected by geometric rearrangement. In this regard, the n → 3s transition is simpler to interpret than, for instance, the $n \rightarrow \pi^*$ transition because the Rydberg electron probably has a minor effect on the chemical bonding. The major effect is the removal of the nonbonding electron.

The spectra in Figures 1 and 2 show very clearly the relationship discussed above. Those molecules which have transition energies close to that of cyclohexanone exhibit little vibrational excitation, reflecting the small change in geometry upon exciting the 3s level. Alternatively, molecules with transition energies shifted substantially to the red, such as the α-substituted isomers in Figure 2, exhibit a dramatic increase in vibrational excitation. It has been shown from ^{13}C NMR studies that α-methyl substitution adjacent to a carbonyl group results in a steric interaction.[6] This is supported by the spectra in Figure 2 since the extensive excitation of the low-frequency modes demonstrates that these molecules undergo a significant change in geometry due to ring rearrangement in the excited state.

The 3s spectrum of the 2-ethyl isomer **9** has a very weak origin peak, labeled with an arrow in Figure 2, whose assignment was confirmed by scanning the spectrum at several temperatures. This is easily accomplished by adjusting the backing pressure of the molecular beam (higher pressures resulting in more effective cooling). The spectrum was determined to be free of hot bands since the intensity of all peaks in the vibrational envelope remained constant over a range of temperatures. Compared to the transition origin of the 2-methyl isomer **8**, the slight red shift and increased degree of Franck–Condon excitation indicates that the 2-ethyl group interacts slightly more with the carbonyl group than the 2-methyl group, consistent with previous studies of relative steric energies.[7,8]

The gap between $\Delta v = 1$ and $\Delta v = 2$ of the vibrational progression observed in **9** is interesting because it is the only such example of a break in the relatively consistent spacing of this low-frequency mode. A possible explanation for this unusual vibrational structure could be the following: In the ground state, the 2-ethyl group may have sufficient interaction with the carbonyl group to red shift the 3s transition origin significantly but not enough to cause the ring to flip to the higher energy twisted form.[9] It is likely that the excited state potential surface exists as a double well with a barrier of inversion between the chair and twist conformation. If the energy of a vibrational mode (i.e., $v = 2$) is located near the top of the inversion barrier, this band would be strongly perturbed. Spectroscopically, this peak might then experience either a large energy shift or even completely disappear.

The spacing between the low-energy bands of all the cyclic ketones substituted at the α-carbon position show similar but unequal spacing, normally increasing for the first few levels and then decreasing in the highly excited vibrations. For example, the spacing between the first four peaks of **8** are 85, 90, and 88 cm^{-1}, respectively. The largest vibrational excitation appears in **13** which displays a progression of 78, 81, 89, 87, and 84 cm^{-1}. This shows that the vibrational potential well is not harmonic but has a quartic component, clearly suggesting that this low-energy ring-bending motion[5] is hindered by repulsive interactions.

Though stereoisomers **10** and **11** were not physically separated from each other, the 3s spectrum of the mixture clearly shows the origin of two distinct species. This same overlapping of spectra is also observed in a mixture of isomers **12** and **13**. The assignment

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(6) Stothers, J. B.; Tan, C. T. *Can. J. Chem.* **1974**, *52*, 308.

(7) Servis, K. L.; Bowler, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 3392.

(8) Allinger, N. L.; Tribble, M. T.; Miller, M. A. *Tetrahedron* **1972**, *28*, 1173. Note: There appears to be an error in Table III in which the calculated ΔH_f° and strain energies of the *cis*- and *trans*-3,5-dimethylcyclohexanones are reversed (see ref 17).

(9) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982; p 212.

of these transitions to particular structures will be discussed in the next section.

B. Cyclopentanone Methyl Isomers. Interpretation of the cyclopentanone spectra is complicated by the fact that the five-membered ring is a nonrigid structure. Therefore, the ring is capable of reorientation in the ground state to relieve steric repulsions resulting from substituent interactions. In contrast, the rigid chair form of the six-membered ring remains fixed, except under extreme circumstances,[10] so conformational assignments are more certain.

The 3-methyl isomer **15** shows very little intensity in the vibrational modes of the 3s state, while the spectrum of the 2-methyl isomer **18** displays a higher degree of excitation. Comparison of **18** to **8** reveals that the transition origin of the cyclopentanone 2-methyl isomer is less red shifted, and the excitation of the low-frequency vibration is greatly reduced. This indicates that the geometric reorientation in the excited state is less than that experienced by 2-methylcyclohexanone. In the latter case, the methyl group must either eclipse the carbonyl group in the ground-state structure or orient itself axially, an energetically unfavorable option. In 2-methylcyclopentanone, however, the twisted ring structure is such that the α-methyl group does not eclipse the carbonyl group,[15b] apparently resulting in less nuclear displacement upon electronic excitation.

The low-frequency ring vibrations of the *cis*-3,4-dimethyl isomer **16** show excitation which can be attributed to the nonbonded repulsions between the adjacent methyl groups. The axial–equatorial interaction of adjacent groups in the puckered five-membered ring cannot be avoided as effectively as in the nearly perpendicular orientation of neighboring cis methyl groups in the chair conformation of cyclohexanone. The rather wide band centered at 397.25 nm (labeled with an arrow in Figure 3) is especially interesting because the peak is actually a triplet with spacing of about 7 cm^{-1}. Since this band can be assigned as one of the ring torsion modes[5,11] (perhaps twisting of the ring bond between the two methyl groups), the triplet structure could be due to three possible orientations of opposing hydrogens on the adjacent methyl groups.

IV. Discussion

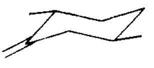
A. Spectroscopic Shifts. The correlation between the electronic transition energy and molecular structure has been studied for many different chromophores, such as Woodward's rules for predicting the alkyl substitution on dienes.[12] There is ample evidence to suggest the existence of such a relationship in the n → 3s transition. This connection between structure and spectroscopic energy will be developed by using the energy shifts of the cyclohexanone monomethyl isomers, whose conformations are known, to predict the transition energies of the dimethyl isomers by simply summing the effects of all methyl groups on the ring. Since these shifts correlate with relative ground-state energies (discussed in the next section), blue-shifted isomers reflect more stable ground-state structures while those red shifted have reduced stability.

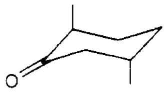
The n → 3s transition origin of unsubstituted cyclohexanone (**1**) will be used as a reference point for all of its methyl isomers (50 717 cm^{-1}). Except for the relative energies of several vibrational bands, the 3s spectra of **1** and the 4-methyl isomer **2** are practically identical. The 7-cm^{-1} difference in their 3s transition energies suggests only slight influence by the equatorial 4-methyl group on the carbonyl chromophore.

The lowest energy conformation of *cis*-3,5-dimethylcyclohexanone (**5**) is the diequatorial form. If the steric energies are strictly additive, the shift of the 3s origin should be twice that of the equatorial 3-methyl isomer **3** (290 cm^{-1}). The observed shift is found to be somewhat less than this value (238 cm^{-1}). The band origin of the trans isomer **4**, which must orient one methyl axially, is red shifted from the cis isomer by 491 cm^{-1}. The steric effect of a single axial methyl group can now be calculated directly by taking the transition energy difference between **4** and the monosubstituted 3-methyl isomer **3**, a difference of 398 cm^{-1}.

By using the experimental energy shifts discussed above, the approximate transition origins of the *cis*- and *trans*-3,4-dimethyl isomers (**6** and **7**) can be predicted. The cis structure should exist in the axial 3-methyl:equatorial 4-methyl conformation since here there is only one transannular methyl-hydrogen repulsion. The equatorial 4-methyl group red shifts the origin only 7 cm^{-1}, while the axial 3-methyl group was found to contribute an additional red shift of 398 cm^{-1}. By using negative energies to represent red shifts, (−7) + (−398) cm^{-1} is added to the cyclohexanone reference energy of 50 717 cm^{-1}, resulting in a predicted transition at 50 312 cm^{-1}. The actual transition origin is found at 50 321 cm^{-1}. The origin of the trans isomer **7** (3 equatorial:4 equatorial) is expected to appear at about the same energy as the 3-methyl isomer **3** (50 862 cm^{-1}) since equatorial 4-methyl substitution scarcely affects the transition energy. The experimental transition energy for **7** is 50 853 cm^{-1}.

The red shift resulting from equatorial 2-methyl substitution (structure **8**) is found to be −546 cm^{-1}. By using this value and those obtained from substitutions at C3, the transition of each component in the *cis*- and *trans*-2,5-dimethylcyclohexanone mixture can be assigned. Consider first the two conformations of the trans isomer

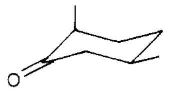

10a


10b

Of the two possibilities, **10a** would be the minimum energy conformation since both methyl groups are oriented equatorially. To calculate the transition energy, (+145) + (−546) cm^{-1} is added to the reference value, resulting in a predicted transition at 50 316 cm^{-1}. The energy for one of the origin peaks observed in the cis/trans mixture is found to be 50 327 cm^{-1}. Therefore, this transition has been attributed to that of the trans isomer. C-13 NMR results[6] support this conformational assignment.

Two conformations are also possible for the cis isomer


11a


11b

NMR data have shown that the most stable conformer is **11a** with its 5-methyl group oriented axially and the 2-methyl group oriented equatorially.[6] The predicted shift for this structure is (−398) + (−546) cm^{-1}, so the origin is expected to appear at 49 773 cm^{-1}. The experimental value is 49 750 cm^{-1} which agrees very well with the predicted transition energy of isomer **11a**. Though not observed in the spectrum, the less stable conformer **11b** should have a transition energy to the red of 49 750 cm^{-1}. From this information, we can determine a lower limit for the shift associated with the highly repulsive axial 2-methyl group. The predicted red shift of something greater than −967 cm^{-1} for **11b** would be comprised of the equatorial 3-methyl group (+145) plus the contribution from the axial 2-methyl shift. Thus, the latter shift is expected to be at least (−1112) cm^{-1}.

The 2,6-dimethyl isomers **12** and **13** can be treated in a similar manner. The diequatorial cis structure **12** has been shown to have the lowest ground-state energy.[13] According to the model, two equatorial methyl groups adjacent to the carbonyl group should experience approximately twice the interaction energy as the monomethyl isomer **8**. Twice the red shift of a single α-methyl group would be −1092 cm^{-1}, yielding a predicted transition origin at 49 625 cm^{-1}. This energy is somewhat lower than the observed

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(10) Djerassi, C.; Warawa, E. J.; Berdahl, J. M.; Eisenbraun, E. J. *J. Am. Chem. Soc.* **1961**, *83*, 3334.

(11) Kartha, V. B.; Mantsch, H. H.; Jones, R. N. *Can. J. Chem.* **1973**, *51*, 1749.

(12) Woodward, R. B. *J. Am. Chem. Soc.* **1941**, *63*, 1123. Woodward, R. B. *J. Am. Chem. Soc.* **1942**, *64*, 72, 76.

(13) Rickborn, B. *J. Am. Chem. Soc.* **1962**, *84*, 2414.

transition at 49 756 cm^{-1} which suggests that the addition of two symmetrically equivalent groups on the six-membered ring does not quite double the energy shift observed in the monosubstituted isomers. A similar effect was observed in the spectrum of *cis*-3,5-dimethylcyclohexanone (**5**). The trans isomer **13** forces one α-methyl group into the axial position, generating a large transannular repulsion with axial hydrogens on C4 and C6. Adding the lower limit of the axial 2-methyl shift (−1112 cm^{-1}) to the equatorial 2-methyl shift (−546 cm^{-1}), we would expect this transition to occur around 49 060 cm^{-1}. Observation of the second transition origin far to the blue of the expected value (49 446 cm^{-1}) therefore suggests a substantial change in conformation such as the conversion into a twisted form, shown by molecular mechanics calculations to lie only 2.72 kcal (about 950 cm^{-1}) above the chair form.[8] A basic premise of the additivity relationship observed in the n → 3s energies will be that the backbone conformation remains constant among substituted structures.

The n → 3s data suggest that nonbonded interactions such as methyl-hydrogen repulsions and the resulting stress on the ring structure are accounted for in the electronic transition energy of the carbonyl group. The additive nature of the spectroscopic shifts in the rigid cyclohexanone ring system demonstrates that by measuring the transition energy of the lone pair electron, the subtle stereochemical effects of the entire ring system can be characterized. This follows from the fundamental principles of perturbation theory which predict that changes in energy levels and wave functions are pairwise additive.[14] It is well established in ^{13}C NMR spectroscopy that the electronic environments of ring structures are changed by small distortions of the molecular skeleton. The more rigid the structure, the better the additivity of substituent effects, thus giving rise to predictable chemical shifts. These concepts apparently apply to the shifts in the n → 3s energies.

Consider next the methyl isomers of cyclopentanone. The origin of **14** will be used as the reference for these structures since all energetic and strain effects of the reduced ring size have already been accounted for in its red-shifted 3s transition, leaving only variations due to substituent and conformational perturbations. The 3-methyl isomer **15** is blue shifted 240 cm^{-1}. Like dimethyl substitution at symmetrically equivalent ring positions on cyclohexanone, the origin of the *trans*-3,4-dimethyl isomer **17** (50 523 cm^{-1}) is shifted slightly less than twice that observed in the monomethyl isomer **15**. Ground-state microwave studies of **15** have verified that the monomethyl isomer retains the twisted form of unsubstituted cyclopentanone[15a] so it is reasonable to assume that both methyl groups in **17** are equatorially oriented. The transition origin of the cis isomer **16** is red shifted from the trans form by −444 cm^{-1}, probably due to the interactions between the axial methyl and ring hydrogens as well as those between the adjacent methyl groups. Consequently, the origin of **16** (50 079 cm^{-1}) is located quite close to that of cyclopentanone (50 068 cm^{-1}). Structures **14** and **16** can be distinguished, however, by differences in their vibrational fine structures as well as by their respective chromophore symmetries, discussed in section C in which polarization effects are considered.

The spectra of the 2,4-dimethyl isomers **19** and **20** again represent a mixture of cis and trans configurations though the assignments are somewhat ambiguous. The large peak at 401.6 nm (49 801 cm^{-1}) is attributed to that of the trans configuration **19** by considering the energetic differences between cis and trans isomers of 2,4-dimethylcyclopent*ane*.[16] In that system, the trans form was found to be 0.3 kcal less stable than the cis isomer due to the axial orientation of one substituent. A larger red shift is therefore expected for the trans isomer if the relative cis/trans stabilities experienced by the ketone and alkane are comparable. The other intense band located at 398.5 nm at first glance appears to be the origin of the cis isomer **20**, but we have instead assigned the peak located at 400.4 nm (49 956 cm^{-1}) as the origin for several reasons. First, the energy of this small peak relative to the trans isomer is blue shifted by 155 cm^{-1} (0.44 kcal), consistent with the relative stabilities of the methylcyclopentanes. Second, NMR measurements indicate that the cis isomer exists predominantly in the diequatorial conformation[6] so the shifts of the monomethyl isomers (**15** and **18**) may be useful in predicting its transition origin. A recent microwave study of 2-methylcyclopentanone[15b] indicates that this structure retains the twisted conformation of the parent ketone with the methyl group oriented equatorially. A transition energy of 49 931 cm^{-1} is found by summing the equatorial 3-methyl (+240) and 2-methyl (−377) shifts. This calculated energy is within 25 cm^{-1} of the smaller peak assigned as the transition origin. The band observed at 398.5 nm is believed to be an abnormally intense vibrational peak of the trans isomer.

B. Ground-State Energies. Having discussed the relationship between specific configurations and the n → 3s transition energy, it seems reasonable to compare these spectroscopic shifts to known ground-state energies. The source of the energy shifts cannot be answered definitively by the available data. However, there is a clear prescription of how to proceed and sufficient information to suggest reasonable hypotheses. If the precise heats of formation of these molecules were known, groups of isomers could all be placed on an absolute heat of formation energy scale. The measured n → 3s energies could then be used to determine the absolute energies of the 3s Rydberg states. The observed transition energy shifts would be easily correlated with either the differences in the ground-state energies or the excited state energies or a combination of the two. Unfortunately, a comprehensive study on the heats of formation of cyclohexanone and cyclopentanone methyl isomers is not available, so this sort of analysis cannot be carried out at this time. However, molecular mechanics calculations have been performed on a variety of cyclic ketones[8] while thermodynamic techniques have been applied to selected epimers[17] so that relative energies between a number of the methyl isomers of cyclohexanone have been determined. The experimental data will be considered first.

Solution phase equilibration studies of the trans → cis epimerization of 3,5-dimethylcyclohexanone have indicated that the cis conformer **4** is 1.3 kcal/mol lower in energy than the trans isomer **5**.[17] This ΔH value was obtained from the measured ΔG by using an approximate ΔS of epimerization. The observed difference in the 3s transition energies of **4** and **5** (491 cm^{-1} or 1.41 kcal) is quite close to the experimental ΔH measurement, indicating that virtually the entire transition energy difference arises from the ground-state energetics.

The energy difference between *cis*- and *trans*-2,6-dimethylcyclohexanone was found to be 1.8 kcal/mol[13] though alternate experimental values range from 1.3 to 2.0 kcal.[18] All of these values, however, are somewhat larger than the measured difference between the transition energies (0.89 kcal) of isomers **12** and **13**. In this case, the spectroscopic energy gives the correct sign but a reduced energy difference between these stereoisomers, a discrepancy which might be explained by a conformational change of **13** proposed in the previous section. It seems probable that the oribital energy of the 3s electron would change as the backbone shifts to an alternate conformation such as the conversion from the chair to the twisted form of cyclohexanone. Under these circumstances, in using the spectroscopic energies to determine cis/trans configurational energies, one would have to consider both the ground-state stabilities and the change in excited-state energies.

There are a considerably greater number of calculated energies available than those determined by experimental methods. The strain energies of numerous ketones including methyl isomers of cyclohexanone have been calculated by Allinger et al.[8] by using an early edition molecular mechanics program. The ordering of strain energies for the cis and trans configurations of 3,4- and

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3,5-dimethylcyclohexanone correlate reasonably well with our measured 3s transition energies (cis-3,5 is the least strained while cis-3,4 is the most strained). However, the calculated energies also suggest that no additional strain is introduced when a methyl group is substituted at the C2 position, contrary to the trend found in the 3s energies. The origin of this discrepancy can be attributed to the nature of interaction between the carbonyl group and an α-methyl substituent.

Experimental[19] and calculated[20] results have firmly established that a methyl group attached to the α-carbon in open chain aldehydes and ketones prefers to eclipse the carbonyl group. The cause for this alignment has been attributed to a minimization of repulsive forces in addition to a slight attraction between the carbonyl and α-methyl group.[20] An important question to consider is whether the results of the open chain systems can be directly applied to the cyclic structures as has been proposed.[19] The earliest reference to this interaction[21] suggested that a repulsive potential of about 1 kcal/mol would explain the relative stability ordering in a variety of cyclic ketones (referred to as the "2-alkyl ketone effect"). As mentioned earlier, ^{13}C NMR data have also indicated a steric interaction between the carbonyl and α-methyl groups.[6] Our spectroscopic results suggest that the red shift of the α-methyl cyclic ketones is due to a repulsive ground-state interaction. Additionally, the high excitation of the lowest energy ring bending mode confirms that the geometry changes substantially in the 3s state. This relaxation of the ring structure must involve the staggering of the carbonyl and α-methyl groups which are nearly eclipsed in the ground-state chair conformation. If the contrary were true, namely that the ground state is stabilized by the methyl $\leftrightarrow$ carbonyl interaction, the steric energy of the ground state would be reduced compared to unsubstituted cyclohexanone, and a spectroscopic blue shift would be expected. Therefore, in order to explain the observed red shift consistent with an attractive ground-state potential, we would have to reason that the excited state is even more stabilized by this interaction. This situation is inconsistent with the high Franck–Condon excitation of the ring bending mode, definitely indicating repulsion in the excited state. It is still not clear how this apparent local repulsion affects the overall ring strain.

Chesnut et al.[22,23] have recently employed a molecular mechanics approach (MM2) to calculate local steric energies in a variety of molecular systems to predict ^{13}C NMR chemical shifts. Both attractive and repulsive interactions between nonbonded atoms can be determined based upon the local van der Waals interaction components of the total strain energy, which are related to NMR shielding and deshielding effects, respectively. The model for predicting chemical shifts in NMR is based on the following concept: Substituents within a certain radius from the nuclei in question lie in the repulsive region of the van der Waals potential well thereby giving rise to a deshielding chemical shift (β-effect), while those within a further range experience a net attraction resulting in a shielding shift (γ-effect). A consequence of this scheme is that the magnitude of the repulsive force is greater than that of the weaker attraction, so that, as observed in NMR experimental data, β-effects are normally larger than γ-effects.

The calculated van der Waals energies also follow the relative shifts observed in our 3s transition energies. Figure 4 plots the correlation between the local van der Waals energies of the carbonyl carbon[24] and the shifts observed in the n → 3s energy for various equatorially substituted methyl isomers of cyclohexanone and cyclopentanone. Though the magnitudes of the n → 3s shifts are considerably larger than the calculated values, a linear relationship clearly exists. On an absolute energy scale, the data points for the five- and six-membered rings do not fall along the same line due to angular perturbations discussed below, but the shifts relative to each unsubstituted parent structure are found to correlate, indicative of a common physical origin.

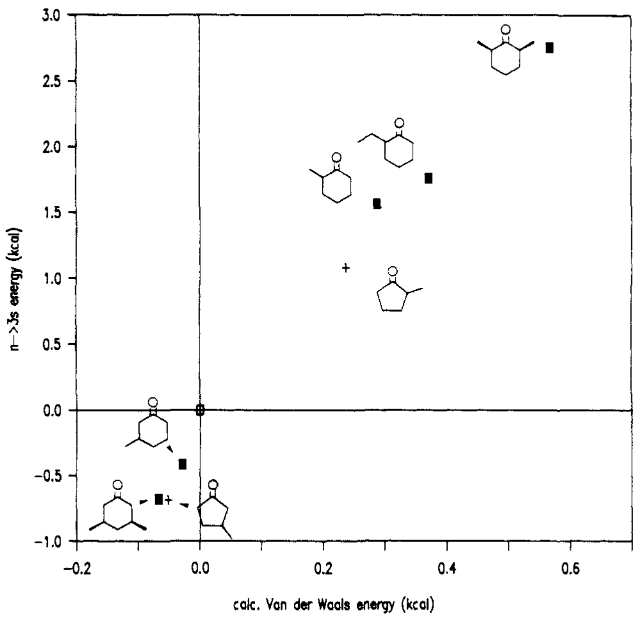

Figure 4. The correlation plot of calculated local van der Waals energies[24] versus the n → 3s transition energy for equatorially substituted methyl isomers of cyclohexanone and cyclopentanone. The unsubstituted five- and six-membered rings were used to define the origin for both the optical transition and van der Waals energies.

The axially substituted isomers were not included in this correlation for several reasons. As shown earlier,[5] the n → 3s transition reflects energetic effects of the C–CO–C bond angle compression is unsubstituted cyclic ketones. The calculated van der Waals energy, however, can only sense angle strain indirectly as a result of geometry optimization. Therefore, even though cyclopentanone is known to have a higher total strain energy, its local van der Waals energy is actually less than that of cyclohexanone.[24] The n → 3s energies are also highly sensitive to the repulsive interactions of axial substituents. Considering only bond type and interaction distance, the local van der Waals energies of axial methyl groups in cyclohexanone are found to be either slightly attractive or negligibly repulsive.[24] Therefore we can reason that the spectroscopic shifts attributed to transannular repulsions are likely due to stress (angular) perturbations of the carbonyl group rather than van der Waals interactions. These strain factors would appear in the *total*, rather than local, steric energy of the molecular mechanics calculation, explaining why the calculated strain energies of the dimethylcyclohexanones,[8] including axially substituted isomers, show the same relative ordering found in the spectroscopic values. The local van der Waals energy calculation provides valuable insight into the subtle interactions of electronic orbitals over multiple σ bonds (long range effects), a feature which is important for the interpretation of NMR chemical shifts as well as the n → 3s transition energies.

As was previously stated, the 3s orbital energies of cyclic ketones appear to be energetically equivalent so that transition energy measurements, at least among structures of similar conformation, reflect relative ground-state stabilities. Such a statement has rigorous meaning when two geometric isomers are compared, such as 4-methyl- and 3-methylcyclohexanone since they have a common heat of formation scale. The meaning is less clear when the two structures are not geometric isomers, as in the comparison of cyclohexanone with any of its methyl derivatives. The carbonyl chromophore, however, is identical in all cases. Spectroscopic energy measurements of the 3s transition can be used to detect subtle perturbations to the chromophore which are a consequence of ring substitution and conformational distortions. The unsubstituted ring is therefore a reasonable energy reference for all of the methyl derivatives. But why should the 3s state be isoenergetic,

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or, stated another way, why should the excited state energy be independent of effects due to ring substitutions? This could be explained by again considering the chromophore and its sensitivity to structure in both the ground and excited states. Extensive delocalization of the lone pair electrons about the ring accounts for sensitivity of this transition to ground-state configurations. The situation is somewhat different for the excited state structure. In the previous study[5] we have shown that the carbonyl group experiences substantial changes as a consequence of electron promotion to the 3s state, resulting in a carbonyl bonding scheme approaching a C–O single bond. Ab initio calculations of the acetone cation[25] indicate that the remaining lone-pair electron is localized on the oxygen atom and therefore does not interact with the rest of the ionic structure. To the extent that Rydberg core geometries are similar to that of the ion, we can draw a similar conclusion about the 3s state. Thus, the 3s energy is not expected to reflect perturbations to the ring structure, resulting in a common energy for all isomers within a given ring size and backbone conformation.

C. Laser Polarization Effects. Polarization effects observed in two-photon transitions can aid in the symmetry assignment of electronic and vibrational excitations.[26,27] The polarization parameter, Ω, is defined as the ratio of peak intensities under circular and linear laser polarization conditions. For rotating symmetric top molecules, the value of Ω can be calculated by using the equation[28]

$$\frac{1}{\Omega} = \frac{2}{3} + \frac{5}{3}\frac{M_0R_0}{M_2R_2} \tag{1}$$

where M_j and R_j are molecular and rotational factors, respectively, in which the subscripts depend on the changes in the rotational quantum number, J. For instance, $R_0 \neq 0$ for $J = 0$ in Q branches, while $R_2 \neq 0$ for $J = 0, \pm1$, and ±2 in all branches. Normally, $M_0 > M_2$ and $R_0 > R_2$. For electronic transitions between states of different symmetry, $M_0 = 0$ so that $\Omega = 3/2$ and is independent of rotational quantum levels. The same ratio is expected for the O, P, R, and S branches in symmetric transitions ($M_0 \neq 0$ but $R_0 = 0$). The Q branch, however, for symmetric transitions, in which $M_0 \neq 0$ and $R_0 \neq 0$, deviates from the 3/2 value. The resulting value of the polarization ratio is $\Omega < 3/2$.

This polarization effect has been used for determining the symmetry of excited electronic states including the assignment of several Rydberg levels.[29-31] The studies that have utilized this polarization information, however, have tended to focus on symmetric molecules, so that there is little information about its application to low symmetry or chiral molecules. It would appear reasonable that this ratio can also be used to determine the local molecular symmetry of the chromophore in asymmetric molecules. The transition of a p-type nonbonding electron to the 3s orbital in cyclic ketones has been shown to be nearly perpendicular[32] so that $M_0 = 0$. Therefore, the second term in (1) drops out resulting in a calculated polarization ratio of $^3/_2$. This value has been verified for the n → 3s transition origin of the symmetric cyclic ketones studied previously.[5] Since, for the case of asymmetric chromophores, the molecular factors M_j are no longer identically zero, the second term in (1) can influence the ratio of the peak intensities. Within the contour of the 3s transition origin, the O, P, R, and S branches would always show a ratio of $\Omega = 3/2$, but a reduction of chromophore symmetry could sharply increase the intensity of the Q branch under linear polarization conditions, resulting in values of $\Omega < 3/2$. The numerous cyclic ketones investigated in this study exhibit various polarization effects which depend on both the position of the methyl substituent and its orientation with respect to the ring. These polarization effects thus provide additional information about the chromophore and hence molecular symmetry. The values of Ω are given for each methyl isomer along with the transition energy in Table I. These ratios were obtained by measuring the peak heights rather than peak areas since all rotational branches except the Q branch should retain the 3/2 ratio. Evidently, it is also important to consider the temperature at which the peak heights were measured since the intensity of the Q branch observed under linear polarization conditions was found to increase in colder samples. We have no simple explanation for this effect. In any case, the reported values for Ω were all obtained at 300 Torr backing pressure.

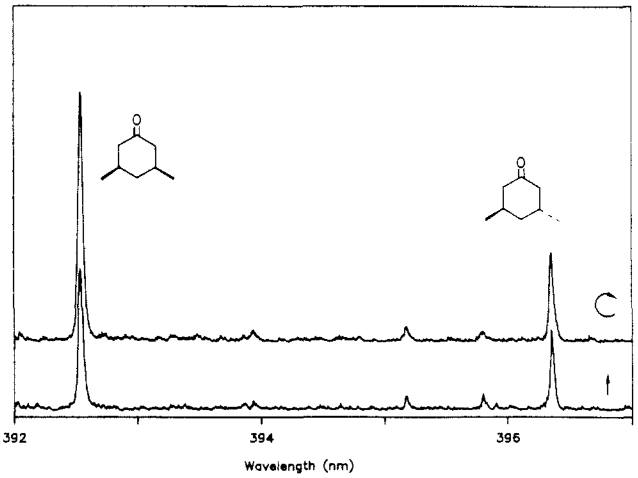

Figure 5. The n → 3s spectrum of a mixture containing cis and trans isomers of 3,5-dimethylcyclohexanone. This illustrates the difference in relative peak heights for each configuration under circular (top) and linear (bottom) laser polarization conditions.

The structures in Figure 1 have Ω values which are consistent with the above symmetry arguments. That is, structures **1**, **2**, and **5** each have C_s symmetry so there is no perturbation to the ring that alters the symmetry of the chromophore. In these cases, Ω has the expected value of 3/2. Even though structure **3** is chiral, its polarization ratio is also $\Omega = 3/2$, indicating that the carbonyl chromophore is not distorted as a result of equatorial 3-methyl substitution. The same 3/2 ratio is found in structure **7**, which is also chiral, and similarly orients the methyl groups equatorially. The only structures in Figure 1 in which Ω deviates from 3/2 is in molecules **4** and **6**. Here, the polarization ratios are 0.9 and 1.3, respectively. A methyl group is axially oriented in each of these isomers so transannular repulsions could slightly alter the backbone symmetry of the cyclic structure.

The polarization ratios of the *cis*- and *trans*-3,5-dimethyl isomers (**4** and **5**) are also useful in assigning each origin peak to a specific epimer based on symmetry considerations alone. The 3s spectrum of a cis/trans mixture under circular and linear laser polarization conditions are plotted in Figure 5. The differences in Ω enable rather simple assignment of the peak at 392.5 nm as the symmetric cis isomer **5** even without knowledge that it is the more stable (hence blue-shifted) structure.

Most of the 2-alkyl isomers in Figure 2 follow the trends in the proposed scheme. As suspected, **8** has a reduced Ω value, indicating a distorted chromophore resulting from the single α-methyl adjacent to the carbonyl group. The origin of **9** is so weak that its ratio is difficult of determine but appears to be approximately 1.0. Epimers **10** and **11** show major differences in their respective polarization ratios. Like **8**, the isomer assigned as the diequatorial trans structure **10** has a low ratio of $\Omega = 0.7$, but, remarkably, the cis isomer **11** has a ratio of $\Omega = 1.5$. The cis isomer **12** has C_s symmetry so the ratio of $\Omega = 1.5$ is not surprising. The trans isomer **13** also exhibits a 3/2 ratio in support of the evidence discussed earlier predicting a twisted (C_2) ring conformation.

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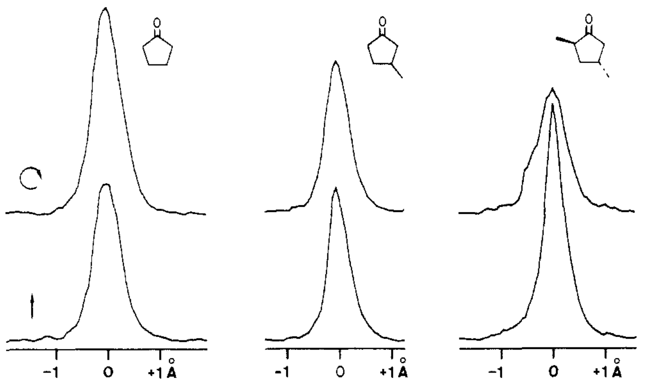

Figure 6. The expanded n → 3s transition origin peaks of cyclopentanone, its 3-methyl and *trans*-2,4-dimethyl isomers contrasting the peak shape under circular (top) and linear (bottom) laser polarization conditions. In determining Ω, the peak heights for each polarization were averaged over many scans.

Since the wave function of acetone's nonbonding electrons is known to have significant density at the α-carbon positions,[33,34] it follows that torsion of the backbone structure of cyclic ketones will distort the HOMO giving rise to the variation in the polarization ratio. It is difficult to predict which methyl substitutions will twist the ring and which have minimal effect on the ring symmetry without more detailed information about the absolute ground-state conformation. Though further evidence is needed to support this claim, it appears that those methyl isomers in Figures 1 and 2 retaining the ratio of $\Omega = 3/2$ exist as the symmetric chair or symmetric twist conformation while those with reduced polarization ratios have varying degrees of asymmetric or distorted backbone structures.

The methyl isomers of cyclopentanone also follow these trends. Structures **14** and **17** have C_2 symmetric producing the expected polarization ratio of 3/2. The ratio observed in **15** is $\Omega = 0.9$ consistent with the results expected from an asymmetric carbonyl group. The polarization ratios of **16**, **18**, **19**, and **20** are all reduced from the symmetric 3/2 value. Figure 6 plots the expanded origin peak of cyclopentanone along with its 3-methyl and *trans*-2,4-dimethyl isomers. This illustrates the progressively distorted ring structures as the geometry departs from the parent C_2 symmetry. In addition to the obvious difference in relative peak heights, the band widths become progressively narrower under linear polarization conditions (bottom series) due to the increasing influence of the Q branch as the structure becomes less symmetric.

It is evident from these polarization studies that the overall chirality of the molecule is not sufficient to cause Ω to be reduced from its value of 3/2 normally observed in the n → 3s 2-photon absorption of ketones. It is rather the symmetry of the absorbing chromophore which is the determining factor. A similar situation exists for another polarization effect, circular dichroism, a method for determining the absolute orientation of a chiral center. In that case, the measured quantity is the difference in absorption peak intensity using right and left circularly polarized light. It follows that those chiral molecules which exhibit a strong CD signal for the n → 3s transition cannot have an Ω value of 3/2 since this behavior is displayed by symmetric molecules. For example, the vapor phase 1-photon n → 3s absorption and circular dichroism spectra of *R*-(+)-3-methylcyclopentanone have been examined.[35] The results demonstrate that the n → 3s transition origin is optically active, consistent with our result of $\Omega = 0.9$. Conversely, chiral 3-methylcyclohexanone would not be expected to have a strong CD signal at the n → 3s transition since our $\Omega = 3/2$ value suggests that the carbonyl chromophore is symmetric. To our knowledge, the gas-phase ultraviolet CD spectrum in the region of the n → 3s transition has not yet been obtained, but its infrared CD spectrum has.[36] That study finds the CD signal for the C=O stretch at 1720 cm^{-1} to be very weak, supporting the contention that the carbonyl chromophore is nearly symmetric.

V. Conclusions

The n → 3s Rydberg spectra obtained by 2 + 1 REMPI have been shown to be highly sensitive to both position and orientation of methyl groups substituted on cyclohexanone and cyclopentanone. The shift in the 3s transition energy, which is found to be additive for multiple substitutions in cyclohexanone methyl isomers, can be related to the ground-state stabilities based on thermodynamic data and molecular mechanics calculations. Furthermore, the n → 3s transition energy reflects the energy of nonbonded interactions enabling the assignment of a spectrum to a particular configuration (and in some cases conformation) of the structure in question. Similar shifts are observed in the methyl isomers of cyclopentanone though the additive relationship remains to be tested. These shifts are believed to originate from the extensive delocalization of the lone pair wave function in the ground state, thereby making the n → 3s electronic transition sensitive to minor changes in ring strain and backbone geometry. Stereochemical effects are thus clearly observed in the energy and vibrational excitations of the sharp Rydberg spectrum.

Laser polarization effects characteristic of two-photon transitions can also be used as a probe to sense changes in molecular symmetry. Structures with C_s and C_2 symmetry experience ionization enhancement under circular polarization conditions ($\Omega = 3/2$). Those structures containing asymmetric chromophores are either less enhanced under circular conditions ($1 < \Omega < 3/2$) or enhanced under linear conditions ($\Omega < 1$). This information is useful in determining the degree of chromophore asymmetry, assigning symmetry to unknown structures, and for uniquely characterizing stereoisomers.

The application of this technique to the study of natural products and biologically important molecules is promising since a number of methods are currently under development which produce cold molecular beams of nonvolatile and thermally labile compounds. Though larger molecules will certainly produce complex electronic spectra, the sharp resonance ionization peaks may prove to be useful in supplementing existing methods of structure elucidation.

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