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2 + 1 REMPI Spectra of Cyclic Ketones in a Cold Molecular Beam. 1. Studies of the n → 3s Rydberg Transition in Unsubstituted Rings

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Abstract: The 2-photon excitation of the 3s Rydberg states in cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, and norcamphor has been investigated by resonance enhanced multiphoton ionization (REMPI). A pulsed and seeded molecular beam of cold sample gas was crossed with a pulsed laser beam from an excimer pumped dye laser. Spectra in the region of 405–380 nm were obtained at sufficient resolution (<1 cm^{-1}) to allow identification of some rotational contours. The C=O stretch and bending modes were identified on the basis of laser light polarization studies (linear versus circular) and by deuterium substitution. In all cases, the C=O stretching frequency was found to occur around 1250 cm^{-1} in the Rydberg spectrum which is significantly reduced from its ground-state counterpart. This reflects the increased C=O bond distance in the excited electronic state. A correlation between the origin of the n → 3s transition energy and the ground-state C–CO–C bond angle was found.

I. Introduction

Resonant multiphoton ionization of molecules cooled in a supersonic expansion has proven to be a useful technique for studying the spectroscopy of excited-state neutrals as well as a source of selective ionization for TOF mass spectrometry.[1-12] Many of the recent MPI studies have used a 2-photon ionization scheme through low-lying excited states.[9-12] This technique has the advantage of very high ionization rates with little or no fragmentation of the molecular ion. While shown to be sensitive to molecular structure and generally applicable to many different molecular systems, the low-lying resonant states are valence in character and usually reflect structure of antibonding states. The higher level Rydberg orbitals, on the other hand, are nonbonding in character. Since cyclic ketones are rigid structures, they are especially good candidates for study with MPI because their excited states have fewer relaxation pathways than open-chain structures. The 3s Rydberg states of many cyclic ketones have transition energies accessible by 2-photon excitations followed by a third photon of the same color to produce ionization. In addition, these states can usually be excited by light at wavelengths longer than 375 nm thereby eliminating the need to frequency double the dye laser output. These optical transitions follow 2-photon selection rules which are complimentary to those of single-photon transitions in symmetric molecules. Among these are g → g rather than g → u selection rules and different laser polarization effects which govern ionization rates in multiphoton transitions.[13]

The n → 3s transition of the carbonyl chromophore, which has already been studied with MPI in acetaldehyde,[14] serves as a reasonable starting point for the systematic characterization of larger, biologically interesting compounds. The initial goal of this study was to examine several low-lying Rydberg states of small organic compounds in order to use the sharp structure of the excited state as a fingerprint for analytical applications. However, the energy and fine structure of the n → 3s transition contained so much information about both the ground and excited states that the focus of this first study is the spectroscopic characterization of the n → 3s Rydberg transition in a variety of cyclic ketones. These results will later be applied to the determination of the transition's sensitivity to subtle changes in molecular structure.

II. Instrumental Section

The resonance-enhanced MPI spectra were obtained with a Lumonics excimer pumped dye laser held at constant intensity over the entire dye output with a microprocessor controlled feedback loop coupled to a Scientech calorimeter. The laser intensity was adjusted with a mechanical flag inserted into the path of the excimer beam so that the

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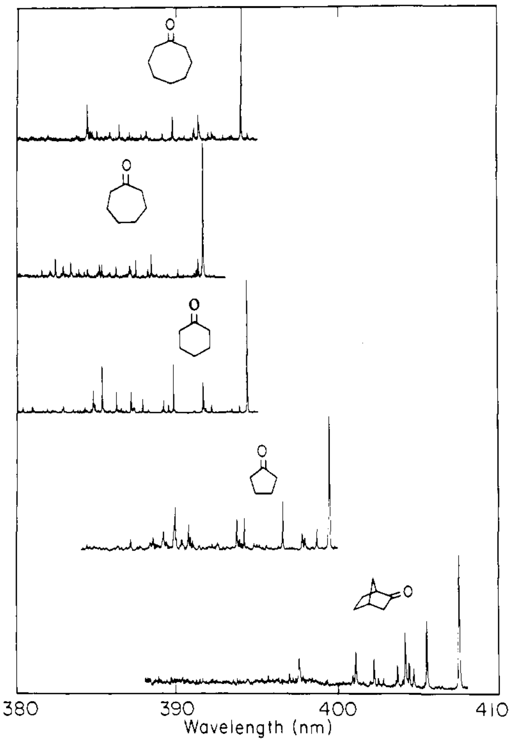

Figure 1. The 2 + 1 REMPI spectra of the n to 3s transition as a function of wavelength for various cyclic ketones in a cold molecular beam. The equivalent one-photon energy for the same transition is obtained by dividing the wavelength by two. The cyclopentanone spectrum was produced with linearly polarized light while the others were produced with circularly polarized light.

dye-laser intensity could be maintained at 500 μJ per pulse. Laser polarization was accomplished in three stages with optics purchased from Karl Lambrecht. A calcite prism, employed to produce pure plane polarized light, was followed by a half-wave plate consisting of 2 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 50 mm diameter lens with a 25 cm focal length, producing a medium-tight focal cross-section.

The molecular beam was produced with a Laser Technics 203 pulsed valve which has a 150 μs pulse duration. All samples were purchased from Aldrich and used without further purification. Samples were introduced by first freezing them in liquid N_2 and then allowing the vapor to evaporate at room temperature into the inlet system maintained under 10–50 Torr of argon. After equilibration, approximately 1 atm of argon was backfilled into the system to produce 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. The supersonic expansion produces a molecular beam with rotational temperatures of less than 10 K. In addition, the vibrational degrees of freedom were cooled sufficiently to prevent the observation of hot bands even for the low-frequency (100 cm^{-1}) vibrations.

For most of the experiments reported here, only the total ionization signal was desired. This was recorded most efficiently by detecting the electrons under a high draw-out field of 1000 V/cm which yielded a strong signal, yet was still much less than the 10^6 V required to field ionize the 3s Rydberg state. The advantage of electron detection over ion detection is that all of the signal can be recorded within a 6-ns window thereby increasing the signal-to-noise ratio. Tests showed that electron and mass analyzed ion detection gave the same MPI spectrum. The electrons were first accelerated to 300 eV followed by a drift of 10 cm and detected with a chevron microchannel plate. The window of a Stanford Research SR250 gate integrator was delayed by 10 ns after the laser pulse which minimized the effects of scattered light and electrons in the total electron signal. The signal pulse was processed 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 thereby minimizing data collection time.

III. Results and Discussion

Figure 1 shows the 2 + 1 MPI spectra through the 3s Rydberg intermediate of the 5-, 6-, 7-, and 8-membered cyclic ketones as well as of bicyclic norcamphor. In contrast to the room temperature 1 photon absorption spectra,[15] the jet-cooled REMPI spectra are extremely sharp, showing well-resolved vibrational fine structure. The strong origin peak and the lack of substantial vibrational excitation suggests that the 3s and ground-state geometries are similar. The analysis of the results will be divided into three sections: the 3s electronic transition energy, rotational contour effects, and vibrational levels of the excited state.

Table I. n → 3s Transition Energy (cm^{-1})

cyclooctanone	50 763
cycloheptanone	51 068
cyclohexanone	50 717
cyclopentanone	50 068
norcamphor	49 079

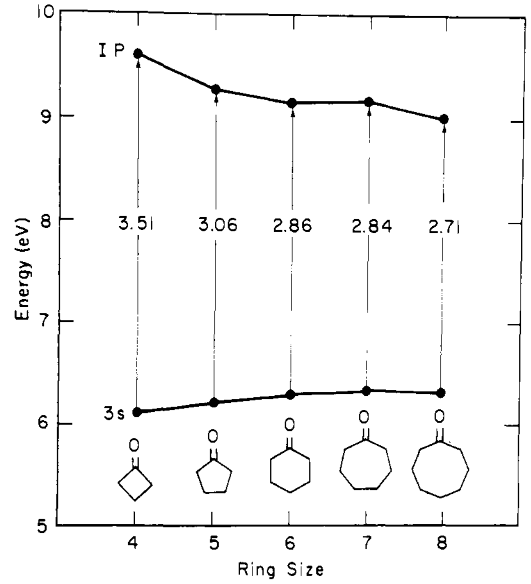

Figure 2. The ionization potential (IP) and the 3s transition energy for the various cyclic ketones. The difference between the two is the 3s term energy.

A. Transition Energy of the n → 3s Rydberg State. Cyclic ketones have little or no molecular symmetry (C_s, C_2, or C_1). Consequently, the n → 3s transitions are allowed in both 1- and 2-photon excitations, each exhibiting strong origin peaks (Table I). In these ketones, the n → 3s transition appears at ca. 50 000 ± 1 000 cm^{-1} depending on the ring size. An important point to consider is whether the excited-state structure, with the electron occupying the atomic-like 3s orbital, more closely resembles the ground-state neutral or the ground-state ion. Normally, the most important factor in determining the relationship between the Rydberg and ionic state is the energy difference between the two, referred to as the term value. Upper level Rydberg states closely resemble the ion since their energies converge to the ionic ground state. Therefore the term values for a particular principal quantum number are expected to remain almost constant among molecules containing similar chromophores. On the other hand, lower Rydberg levels such as the 3s confine the electron to an energy level that is roughly $^2/_3$ the ionization energy. Figure 2 plots the variation of 3s transition energy, the ionization energy, and the resulting term value as a function of increasing ring size. As previously observed,[15,16] there is a gradual decrease in the term value as the rings are enlarged, but this decrease is a consequence of both decreasing IP along with an increasing 3s transition energy. Moreover, it is evident from Figure 2 that the IP variation over the homologous group is close to three times as large as the variation in the n → 3s energy.

Consider first the change in ionization energy as a function of ring size. The IP decreases in larger rings as a result of stabi-

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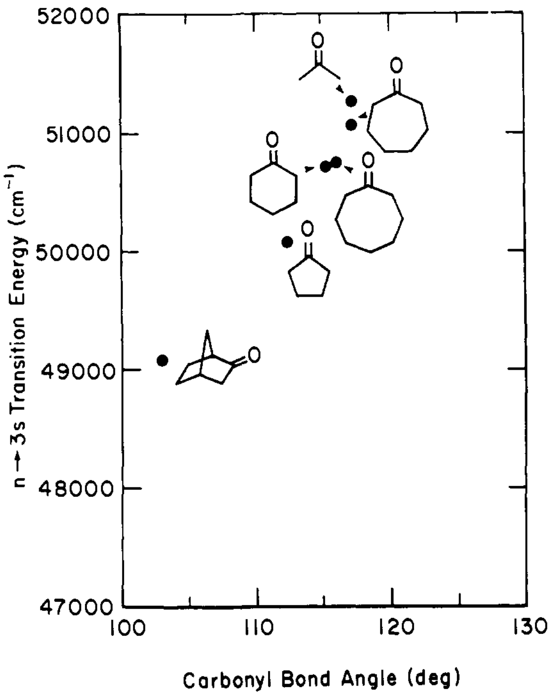

Figure 3. The 3s transition energy as a function of the C–CO–C bond angle.

lization of the positive charge by the methylene groups within the ring. This effect is analogous to the trend toward decreasing IP in progressively larger open-chained ketones[16] with the two series showing approximately the same reduction in ionization potential with increasing number of adjacent methylene groups. Figure 2 shows that the IP is a smoothly varying function that flattens out in larger rings because additional methyl groups far from the absorption chromophore are not effective in accommodating the charge. An exception to the smooth decrease of the IP's is cycloheptanone, which has an IP somewhat higher than expected. This may be a reflection of the 7-membered ring's ground-state stability.

In contrast to the IP's, the 3s transition energy of cyclic ketones *increases* smoothly with ring size from cyclobutanone to cycloheptanone, demonstrating that the n → 3s transition energy follows a trend that is opposite from that of the ionization energies. This is also different from the n → 3s transition of the straight chain ketones which is essentially constant with increasing chain length.[17] Similar to the ionization energies, the 3s variation has an inflection at the 7-membered ring.

It is not clear whether these opposing trends in the IP and the n → 3s transition energies are unique to cyclic ketones. The variable among different ring sizes which closely follows the trend in the 3s Rydberg levels is the decreasing ground state C–CO–C bond angles of the acetone chromophore (Figure 3). In fact, this correlation places the n → 3s energy of the 7-membered ring (3s, 51 068 cm^{-1}, angle = 117.3°[18]) very close to that of strain-free acetone (3s, 51 270 cm^{-1}, angle = 117.2°[19]) even though their respective IP's differ by 0.6 eV. Since straight-chain ketones have approximately the same C–CO–C angle, their 3s energies are expected to be the same as that of acetone, as is experimentally found.[17] The 3s origin peak of cyclohexanone is shifted 351 cm^{-1} to lower energy relative to cycloheptanone and the corresponding carbonyl bond angle from electron diffraction data is found to be reduced to 115.3°.[20] The 5-membered ring, with a carbonyl angle of 112.4°,[21] shifts an additional 649 cm^{-1} to lower energy. The bond angle of 103° used for norcamphor was taken from the equivalent 2-carbon bridge in norbornane[22] since the values are expected to be quite similar.

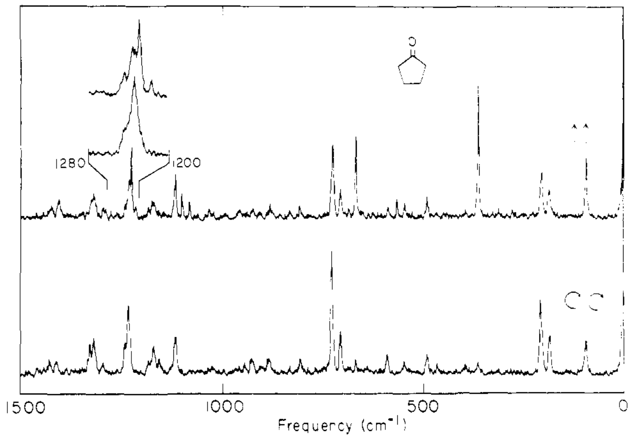

Figure 4. The two-photon 3s spectrum of cyclopentanone with use of circularly and linearly polarized light. The spectrum has been converted from a wavelength to an energy scale with the transition origin serving as the zero point of the energy scale. The top peak in the insert was produced with linear polarization while the bottom was produced with circular polarization.

The origin of cyclooctanone lies between that of the 6- and 7-membered rings. Unfortunately, the electron-diffraction data were not available to verify the C–CO–C bond angle. As a result, we have taken an optimized carbonyl bond angle of 116.1° which was derived in a molecular mechanics calculation of its ground-state vibrational frequencies.[23] This fits well with the observed correlation in Figure 3.

B. **Rotational Effects.** When resonant lifetimes are sufficiently long to observe rotational structure or contours, it is sometimes possible to determine the molecular symmetry of the vibrational mode. A particularly good example of this occurs in cyclopentanone. As shown in Figure 4, the specra obtained with circular and linear laser polarization are strikingly different. Although the ground-state geometry of cyclopentanone is twisted rather than planar, this molecule has a C_2 axis of rotation. In contrast, the 6-, 7-, and 8-membered rings have no rotational symmetry. Furthermore, their spectra under circular and linear polarization do not exhibit the large differences observed in the case of cyclopentanone.

Asymmetric tops, such as cyclopentanone, exhibit vibrational contours of three possible types depending on the symmetry of the vibrational mode.[24,29] A C-type band consists primarily of a Q branch and indicates an out-of-plane vibration in relation to the acetone chromophore. In the 2-photon n → 3s transition, Q branches ($\Delta J = 0$) are not excited by circularly polarized light ($\Delta J = \pm 2$), so that such bands disappear under these conditions. There are several examples of pure Q branches, among them bands at 366 and 671 and several smaller peaks around 1100 cm^{-1}. We assign the 366-cm^{-1} band to be a C=O out-of-plane bend. An A-type band consists of P and R branches with a Q branch of moderate intensity as shown in the insert in Figure 4. This type is associated with a vibration parallel to the axis of rotation containing the C=O group. For the same reason as above, the Q branch disappears with circularly polarized light. The symmetry of this band suggests that this absorption corresponds to the C=O stretch. This assignment is discussed in greater detail in the following section. The final category of vibration is a B-type which represents in-plane modes with the acetone chromophore and exhibits P and R branches but no Q branch. An example of this type would be the C=O in-plane bend which apparently is not excited in the 3s spectrum.

Other bands in the cyclopentanone spectrum, along with all of the vibrational bands of the other cyclic ketones, show less dependence on the laser polarization. This is because only vi-

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brations that are either parallel or perpendicular to the C_2 axis can exhibit pure A-, B-, or C-type rotational contours. The vibrations for most of the other modes in cyclopentanone (at least those excited in the n → 3s transition) are of mixed symmetry with respect to the axis of rotation. Therefore, the rotational contour of the peaks will be various combinations of A-, B-, and C-types. Similarly, the lack of a symmetric rotational axis in the other cyclic ketones leads to vibrational bands of mixed character. In addition, some of the larger ring structures have two or more conformations of similar stability which may exist simultaneously in the cold beam. This could further degrade the distinction between band types. For instance, cycloheptanone is calculated to exist in a mixture of two ground-state geometries.[25] One is a twisted form that has a C_2 rotational axis, while the other, more stable form is also twisted but the carbonyl group occupies the number 2 carbon, thereby eliminating the symmetric rotational axis.

Although the strong dependence on laser polarization is absent for most of the bands in the molecules investigated, there is another effect that remains even for bands of mixed A-, B-, and C-types as well as for the transition origin. This is the ratio of ionization intensity, Ω, between circular and linear laser polarizations in 2-photon transitions. It has been shown that Ω has a value of ${}^3/_2$ for transitions in which the electronic ground and excited states have different symmetries, and $\Omega < 1$ when the respective symmetries are the same.[13] By this means it is possible to determine the symmetry of the excited state as was done, for instance, by Taylor et al.[26] in assigning Rydberg states of *trans*-1,3-butadiene, Berg et al.[27] for the case of benzene, 1,3-butadiene, and 1-azabicyclo[2.2.2]octane, and McDiaramid et al.[28] for states of *cis*-hexatriene.

The n → 3s transitions of carbonyl groups are expected to have $\Omega = {}^3/_2$ since the transition from a p-type nonbonding oxygen electron to a 3s orbital results in a change of symmetry. Indeed, all of the bands studied in these cyclic ketones have $\Omega > 1$ except for some vibrational bands of cyclopentanone in which the enhancement with circular polarization occurs in all but the Q rotational branches. In particular, the value is precisely ${}^3/_2$ for the origin and all vibrational bands of cyclohexanone which has a plane of symmetry.

C. Vibrational Assignments. Only a few vibrational modes in the n → 3s transition are excited, and of those, only the first harmonic appears in the spectrum. In all of the spectra, the origin is the most intense peak, characteristic of a nearly vertical transition. This makes assignment of the bands somewhat easier than in the case of the n → π^* transition in cyclopentanone.[29] In the latter case, substantial nuclear displacement, including pyramidal distortion due to rehybridization of the sp^2 carbonyl group, results in numerous overtone and combination bands as well as inversion doubling in the nonplanar acetone chromophore.

The spectra of Figure 1 are replotted in Figure 5 on an energy axis from 0 to 1500 cm^{-1} with the 0–0 transition energy serving as the common origin. Little structure was detected beyond 1500 cm^{-1}. The identification of these bands has been greatly aided by a knowledge of the ground-state normal modes.[23,30-32] The bands in Figure 5 fall into 2 main groups. Those between 800 and 1500 cm^{-1} normally represent vibrations involving C–H and C–C motions adjacent to the carbonyl group and the C=O stretch. The bands between 0 and 800 cm^{-1} are associated with the low-frequency skeletal vibrations and the C=O bending modes.

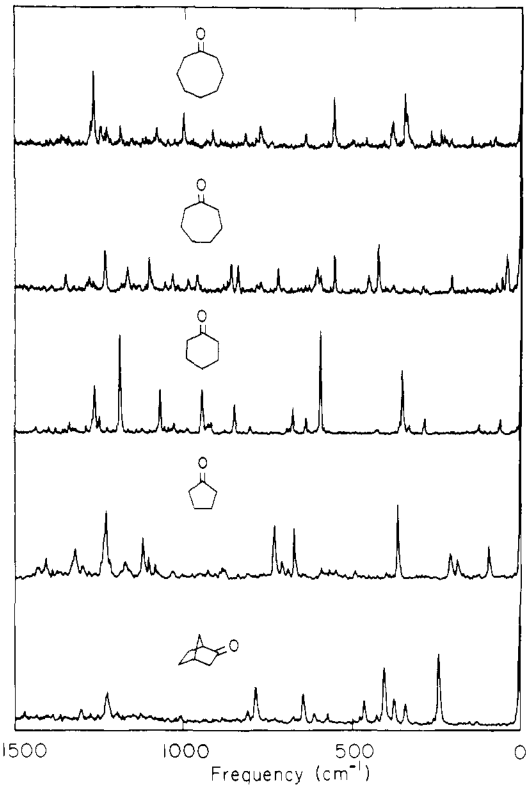

Figure 5. The two-photon 3s vibrational spectra of the various cyclic ketones. The zero for the energy scale is the origin of the n to 3s transition. No significant structure was observed beyond 1500 cm^{-1}.

1. The C=O Stretch and Bending Vibrations. The n → 3s transition involves the excitation of an oxygen atom lone pair electron to a Rydberg orbital. Although the lone pair electrons are formally nonbonding in the hybridized orbital model, they do participate in the bonding when the electronic structure is described in terms of linear combinations of symmetry orbitals. For this reason, the excitation of the symmetric C=O stretch and bending modes is expected in the n → 3s transition. It is therefore surprising that these C=O frequencies in the 3s Rydberg level, as well as the ion, are not yet known.

High-lying Rydberg states have core geometries that differ little from the geometries of the ion to which the series converges. Thus, the ion and the upper level Rydberg state vibrational frequencies are expected to be quite similar. Because the 3s state is the lowest lying Rydberg state, its frequencies, although similar to those of the ion, will not be identical with it. Nevertheless, the comparison between them is very useful in identifying vibrational frequencies. Some time ago, Robin and co-workers compared the 1-photon 3s Rydberg spectrum of acetone and acetone-d_6 with their corresponding photoelectron spectra (PES).[16] They found that upon deuteriation, a broad band at approximately 1200 cm^{-1} shifts to 900 cm^{-1} in both the Rydberg state and the ion. On the basis of this shift, they assigned the absorptions in acetone at 1200 cm^{-1} to the $-CH_3$ deformation and concluded that there is essentially no excitation in the C=O stretch or bending modes which in neutral acetone lie near 1700 and 400 cm^{-1}, respectively.[33]

Robin's interpretation is in conflict with our observation, in the case of cyclopentanone, of an A-type vibration at 1230 cm^{-1}. This transition appears to involve a vibration along the C=O bond axis and therefore could not be assigned to the $-CH_2$ bending modes. In addition, our observation of the sharp C-type band at 366 cm^{-1} strongly suggests excitation of the C=O out-of-plane bend. Since these frequencies are far from their ground-state counterparts (1748 and 450 cm^{-1}, respectively), we conclude that there is a substantial change in the C=O bond length upon excitation to the 3s Rydberg state.

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Table II. Relationship between Carbon-Oxygen Bond Length and Stretching Frequency

	C-O bond length (Å)	freq (cm^{-1})
$H_2C{=}O$	1.208[a]	1744
$(CH_3)_2C{=}O$	1.214[b]	1697[c]
$H_2C{=}O^+$	1.234[d]	1590[e]
$(CH_3)_2C{=}O^+$	1.302[f]	?
$H_2C{=}O$ (π^*)	1.32[g]	1180[g]
HC(O)-OH	1.358[h]	1105[i]

[a] Reference 35. [b] Reference 19. [c] Reference 33. [d] Reference 36. [e] Reference 37. [f] Reference 34. [g] Reference 38. [h] Reference 39. [i] Reference 40.

In support of the C=O stretch and bend assignments of the 1230- and 366-cm^{-1} bands, we turn to some ab initio calculations of the acetone ion geometry. The C=O bond distance, which is 1.21 Å in the ground-stage neutral, shifts to 1.30 Å in the ion.[34] The C=O bond distance in the ion is thus approaching a C-O single bond in an sp^2-hybridization scheme such as that found in the ground state of formic acid (C-OH bond length = 1.358 Å) for which the frequency is 1105 cm^{-1}. With such a large change in the bond length, the C=O stretch should be excited upon ionization, and thus probably also in the n → 3s transition. In this connection, it is helpful to consider the situation for the case of formaldehyde in which the C=O stretching frequency can be assigned unequivocally because there are no C-H modes to interfere with their observation. The bond distances and vibrational frequencies of formaldehyde neutral and ion, shown in Table II, were established either from experiments or from ab initio calculations. It is evident that the 0.026-Å change in the C=O bond distance is accompanied by a 154-cm^{-1} reduction of the C=O vibrational frequency. If we assume an inverse relationship between the bond distance and vibrational frequency while using ground- and excited-state data of formaldehyde, acetone, and formic acid as a guide, we predict that the C=O stretch in the acetone ion would appear around 1250 cm^{-1}. This is approximately where we observe it in the 3s spectra of the cyclic ketones.

In order to verify our assignment of the C=O stretch in the 3s Rydberg state, we obtained the spectrum of cyclohexanone-*2,2,6,6-d*$_4$. The spectra for the normal and isotopically labeled compounds are shown in Figure 6. Nearly all of the peaks in the region between 800 and 1300 cm^{-1} are substantially shifted to lower energy thereby identifying them as having a large C-H bend component. A notable exception is the small fundamental peak at 1255 cm^{-1} which shifts by only 23 cm^{-1}. We assign this band to the C=O stretch mode and note that it is rather hidden in the C-H bending modes. In cycloheptanone, the band at 1278 cm^{-1} has been tentatively assigned as the C=O stretch. Cyclooctanone has a sharp peak at 1262 cm^{-1} which we also believe to be the C=O stretch. Highly rigid norcamphor has a moderately intense C=O stretch at 1227 cm^{-1} unobstructed by C-H modes since the α carbons are rendered asymmetric by the bridgehead.

The conclusion drawn on the basis of the data in Figure 6 is similar to that reached by Robin for the n → 3s transition and the PES of acetone, which is that most of the bands near 1200 cm^{-1} can be assigned to the C-H bending motions. However, the improved resolution of our spectra, obtained in a cold beam, shows that the C=O stretch is in this spectral region as well. Its considerable shift from the ground-state value parallels the shift in the lower frequency C=O bend. Furthermore, the fact that nearly all of the bands shift upon deuteration of the α carbons indicates that excitation is largely localized to vibrations close to the carbonyl group.

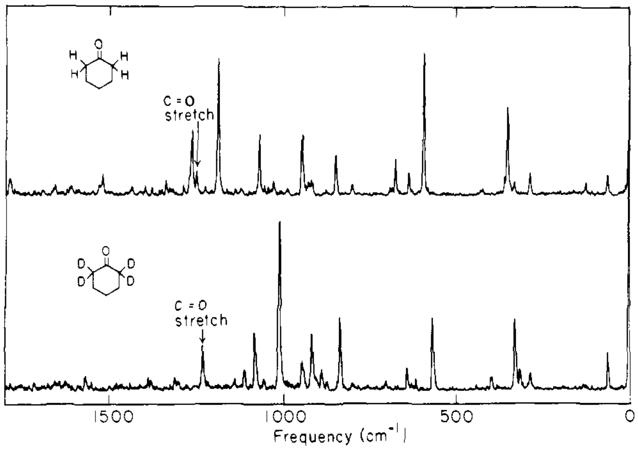

Figure 6. The two-photon 3s spectra of normal and partially deuteriated cyclohexanone. Both spectra were produced with circularly polarized light.

2. The Acetone Chromophore Geometry and Its Effect on Ring Vibrations. Our results indicate that there is substantial relaxation of the C=O bond length upon exciting the 3s Rydberg state. This raises the question of the carbonyl group planarity in the excited state. According to vibrational analysis on the 3s state of acetaldehyde,[14] this molecule remains planar in the excited state. On the basis of this and the absence of any evidence of inversion doubling in any of our data, we conclude that there is no pyramidal distortion in the 3s excited state such as that observed in the π^* state.

Another trend observed in Figure 1 is the inverse relationship between the ring size and the intensity of the vibrational bands in the spectrum. This effect can be related to the reduction of angle strain upon excitation of the 3s Rydberg state. That is, the increase in the number and intensity of low-frequency ring modes in the more highly strained rings can be explained by the relaxation of the sp^2 hybridization in the carbonyl chromophore. Since the 7-membered ring has virtually no tension in the C-CO-C bond angle, there is no stabilization in the excited state due to release of strain. Consequently the transition energy is much like that of acetone and the ring modes remain largely unaffected during the transition. On the other hand, molecules such as norcamphor experience substantial stabilization by relaxation of the carbonyl group. This reduced electronic energy is accompanied by a geometric rearrangement which excites the ring modes most sensitive to changes in the acetone chromophore.

The identification of some other peaks in the spectra is also possible. Most of the CH$_2$ motions should be similar to those in the ground state since the C-H bond is not greatly affected by the removal of the oxygen lone-pair electron. As was already mentioned, the major influence of the n → 3s transition on the excitation of the various vibrational modes appears to reflect the change in angle strain. Although there are many common features among the spectra of Figures 1 and 5, each molecule has some unique characteristics. These are discussed below.

Cyclooctanone. Only a few vibrational modes are excited in the 3s spectrum of cyclooctanone. We have assigned the strong band located at 1262 cm^{-1} as the C=O stretch. The sharp band at 551 cm^{-1} is probably the C=O out-of-plane bend reduced from the ground-state value of 602 cm^{-1}. This molecule is known to be somewhat rigid due to transannular strain which is apparent from the lack of very low energy ring modes below 100 cm^{-1}. The remaining bands in the spectrum are difficult to assign due to the large number of possible vibrations.

Cycloheptanone. The 3s spectrum of cycloheptanone has little intensity in its vibrational bands, indicating that either few of its vibrational modes are symmetric or that there is virtually no change in geometry between the ground and excited states, both of which are likely. The C=O stretch and C=O bend can

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probably be identified with the bands at 1278 and 552 cm^{-1}, respectively. The comparison with the ground-state vibrational spectrum indicates that other active modes include the C–H rock (423 cm^{-1}) and C–H wag (1233 cm^{-1}). There are also at least 5 bands below 60 cm^{-1} which reflect the complicated pseudorotation pathways of a non-rigid structure.

Cyclohexanone. The chair conformation of cyclohexanone is rigid and has a plane of symmetry through the acetone chromophore resulting in strong excitation of several vibrational modes. Comparison of its electron diffraction data[20] to that of cyclohexane indicates that the carbonyl end is less puckered while the opposite end is more puckered due to the slight additional strain inflicted by sp^2 hybridization. In the 3s spectrum, the C=O stretch occurs at 1255 and the C=O bend at 599 cm^{-1} reduced from 1718 and 655 cm^{-1} respectively in the ground state. Since the α-carbon C–H modes (800 to 1300 cm^{-1}) are moderately excited it seems likely that the carbonyl end reorients slightly as a result of the weakening of the sp^2 character. This is supported by the appearance of the band at 358 cm^{-1} which is assignable as the C–CO–C bond angle compression reduced from 411 cm^{-1} in the ground state. There is also very slight excitation of the two symmetric ring bending modes at 63 and 130 cm^{-1}.

Cyclopentanone. As discussed earlier, the rotational effects enable more specific vibrational assignments based on symmetry considerations. The bands remaining after identification of the C=O stretch and bend (1230 and 366 cm^{-1}) are straightforward to assign since there are only a few possible ring modes. Clearly seen at 95 cm^{-1} is a pseudorotation band. The two peaks centered at 200 cm^{-1} (B-types) can be assigned as ring torsion modes though only one such band was assigned in the ground state.[30] Located at 671 cm^{-1} is a sharp band (C-type) while at 729 cm^{-1} is a broader band (B-type) which are likely associated with (CO)–C stretching and C–H wagging modes though the exact assignment is uncertain due to the presence of multiple peaks in this region of the ground-state spectrum.

Norcamphor. This bicyclic ring is a highly strained and rigid structure. The lowest energy ring modes, as expected, disappear as a result of the rigid structure accompanied by the appearance of "butterfly" modes similar to those found in norbornane.[41] Also, due to the substitution of the α-carbon by the bridge structure, it lacks the symmetric C–H wagging and bending modes characteristic of the other rings. The single band at 1227 cm^{-1} is assigned as the C=O stretch reduced from 1755 cm^{-1} in the ground state.

D. The n → 3s Transition Energy and Its Effect on Ring Strain. The differences in the n → 3s transition energies among the various cyclic ketones arise from differences in either the stabilities of the ground state or the excited 3s state. As shown in Figure 3, the n → 3s transition energy varies approximately linearly with the ground-state C–CO–C bond angle. Such a correlation appears to result from the relief of angle strain as the electron is promoted to the 3s Rydberg orbital. The low value of the C=O stretch frequency in the 3s state and the excitation of the vibrational modes in the vicinity of the carbonyl group indicate that the geometry of this chromophore is somewhat relaxed relative to the ground state. As already mentioned, the straight chain ketones appear to have similar n → 3s transition energies, presumably resulting from the lack of ring strain. Unfortunately, these transitions have been determined in room temperature 1-photon absorption studies so that their precision is insufficient for lending unequivocal support to this assumption.

If the carbonyl angle strain is reduced or eliminated in the 3s Rydberg state, it is reasonable to assume that a similar relief would be present in the ionic state. Thus the ionization energies of the cyclic ketones should show these trends. In one sense, the trends in ionization energies should be less equivocal because the electron is totally removed. However, as pointed out previously, the ionization energies vary considerably with the number of carbon atoms because of charge delocalization. It is possible to correct for this effect by taking the difference between the ionization energies of each ring and its corresponding open-chain structure containing the same number of methylene groups. However, such an analysis neither supports nor refutes the notion that the strain is relieved upon ionization. The scatter in the ionization energies (0.05 eV; 400 cm^{-1}) and the crudeness in accounting for the charge delocalization evidently mask the sought after subtle differences.

Allinger et al.[42] has calculated total strain in a large number of cyclic ketones by the use of a molecular mechanics program. These calculations, as well as thermodynamic data, indicate that the least strained cyclic ketone is cyclohexanone rather than cycloheptanone. Since the 3s transition appears to be related to angle strain, this discrepancy in relative stabilities can be accounted for in other types of strain, such as transannular and Pitzer strain. The connection between ground-state energies and the 3s transition becomes more interesting in the case of methyl-substituted cyclic ketones. These series of isomers can be placed on a common heat of formation basis so that, in principle, the relationship between spectroscopic and ground-state energies can be studied more quantiatively. This will be discussed in another publication.[43]

IV. Conclusions

This investigation on the 3s Rydberg states of cyclic ketones has shown that the promotion of the oxygen lone-pair electron to the 3s Rydberg orbital has pronounced effects on the molecular geometry. The C=O stretching frequency is reduced substantially from approximately 1750 to about 1250 cm^{-1}, indicating that the C=O double bond takes on characteristics of a C—O single bond in the excited state. However, all of the results suggest that the C–CO–C group remains planar.

Deuterium substitution on the two α-carbons results in a large shift of a substantial number of absorption bands to lower frequencies. This enables the assignment of the C=O stretch band which is shifted only 23 cm^{-1} from its nondeuteriated counterpart. In addition, the n → 3s transition is accompanied by the excitation of several low-frequency modes that can be assigned to ring-bending modes. These observations are consistent with the large change in the C=O bond length and the relaxation of the C–C-O–C bond angle.

The results suggest that the relaxation of the carbonyl group in the 3s Rydberg state releases all or part of the angle strain in the cylic ketones depending upon the ring size. If this can be verified, the measurement of the 3s energy would provide a very accurate and convenient means for determining nonbonded repulsions in substituted cyclic ketones as well as relative stabilities of conformational isomers. Further work in this direction is in progress.

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Registry No. Cyclooctanone, 502-49-8; cycloheptanone, 502-42-1; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; norcamphor, 497-38-1.

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