Vacuum Ultraviolet Absorption Spectra of Methyl-substituted Cyclopentanones and Cyclohexanones

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The vacuum ultraviolet absorption spectra of methyl-substituted cyclohexanones and cyclopentanones are reported and analysed in terms of Rydberg series. Apart from an anomaly in the $n = 4$ region, which is attributed to interference by a molecular valence state, long series are assigned in all cyclohexanone spectra allowing accurate determination of the ionization energies. The cyclopentanone spectra are similar but less extensive. The Rydberg structure differs with substituent position in the length and the type of series that dominates the spectra, and in the width of the individual bands. Two distinct substituent effects are identified; an 'internal pressure' effect causing increased bandwidth and increased Rydberg–valence state interaction; an orbital mixing effect causing transfer of transition intensity from a d-series in the parent molecules to a p-series of the substituted compounds as the substituent approaches the chromophore. The absolute intensities of the spectra are reported and discussed, and molecular orbital calculations on the ground states of the molecules and their ions used to interpret aspects of the spectra. The vibronic structure of the lowest energy, $n = 3s$, transitions of selected compounds both from photoabsorption and resonance-enhanced multiphoton ionization (REMPI) spectra are compared with an REMPI study of cooled molecules.

Well resolved Rydberg series in the absorption spectra of molecules are affected by substitution of the molecules in a consistent manner. The structure rapidly loses intensity and the individual bands broaden, resulting in complete loss of observable Rydberg structure at even moderate extents of substitution. Such behaviour is well documented,[1] but no clear explanation is available. The general impression is that it is the natural consequence of increased molecular complexity; more vibrational modes producing more vibronic transitions, resulting in a general spreading of the weak Rydberg oscillator strength. Whilst perfectly reasonable in terms of valence transitions this explanation is less obvious for Rydberg absorptions which in many cases are highly vertical transitions, with the states not being strongly coupled to the nuclear motions (with the notable exception of the lowest energy states).

In an earlier publication[2] we proposed an alternative explanation namely that the substituents act on the Rydberg states in the same manner as high pressures of inert gases. The gases cause extensive broadening of the Rydberg structure through physical interaction at pressures *ca.* 100 bar,[3] and the 'effective' or 'internal' pressure of substituents located close to a chromophore, estimated from their distances from the chromophore, is many times greater than this. The systems studied in that work, the substituted *para*-benzoquinones, were di-chromophoric and showed clear evidence of substituents only affecting one of the two chromophores. A systematic change from a di-chromophoric to a mono-chromophoric type of spectrum was observed with progressive substitution, with complete loss of Rydberg structure when full substitution was introduced.

In this paper we consider substituent effects on a mono-chromophoric system, the cyclic ketones. Recently we have presented and analysed the extensive Rydberg structure observed in the spectra of cyclopentanone and cyclohexanone,[4] and discussed the lack of structure in the spectra of cyclobutanone and cycloheptanone. The five- and six-

membered rings allow for controlled progressive approach of substituents, methyl groups in this work, to the chromophore, in a manner that was impossible in the benzoquinones. The evidence that this provides for the internal pressure model of the substituent effect on Rydberg structure in absorption spectra is the main interest of this work.

There is very little previous work on these molecules. The lowest energy Rydberg transitions to the 3s orbital have been investigated in detail using REMPI of the molecules cooled in a molecular jet;[5,6] the circular dichroism spectra of 2-methylcyclopentanone of the same transition has been much used as a test case for vacuum ultraviolet circular dichroism measurements;[7] however, the Rydberg structure has never been reported previously.

All Rydberg transitions in these molecules originate from the highest occupied molecular orbital which is non-bonding, composed predominantly of the oxygen $2p_y$ atomic orbital orientated perpendicular to the carbonyl bond, labelled n_O, the composition of which we find from a variety of ground state computational techniques to be very insensitive to methyl substitution of the rings.

Experimental

The spectra were measured on a McPherson 2413 m spectrograph which has a 1200 lines mm^{-1} grating, dispersion 0.27 nm mm^{-1}, using continuum emissions from microwave powered plasmas in rare gases as the light sources. The samples were introduced directly into the spectrograph at a pressure of *ca.* 1×10^{-5} Torr‡ and the spectra were recorded on SWR plates.

The plates were calibrated by fitting the wavelengths of known atomic emission lines, both from a Garton Lamp, Chelsea Instruments, run at low voltage and superimposed on the spectra, and from known impurities present in the lamps, to a quadratic function of their positions on the photographic plates. Plate positions were measured using a Zeiss

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‡ 1 Torr = (101 325/760) Pa.

microcomparator and densitometry was performed using a Joyce-Loebl densitometer.

The spectra were also measured on a photometric spectrometer for the determination of absolute absorption coefficients. This consists of a 1 m Rank-Hilger 776 monochromator with a 600 line mm^{-1} grating, a McPherson 665SS double-beam chamber, a 782 logarithmic ratiometer and a hydrogen discharge lamp. The pressure of the samples was measured using an MKS Baratron and the molar absorption coefficients measured are estimated to be $\pm 10\%$.

Multiphoton ionization spectra were measured using a home-made XeCl excimer laser (constructed at the Institute of Electronic Structure and Laser, Crete) which produced ca. 50 mJ pulses of 12 ns duration, pumping a home-made dye laser. The laser light was mildly focused into a cell containing the sample at 1–2 mbar pressure and the ionization current recorded against the wavelength of the laser. The spectra were calibrated by simultaneously measuring the optogalvanic signal from a hollow cathode lamp.

Samples were purchased from various suppliers and used as supplied.

Molecular orbital calculations were performed using the AMPAC program[8] with full variation of all parameters.

Results and Discussion

Rydberg Series

The assignment of Rydberg series in these spectra was achieved by the same method that we have used for all previous studies. The accurately determined absorption energies, hv, of peaks thought to belong to the same series, usually the longest series observed, are used in the Rydberg formula;

$$hv = E_{i,1} - R/(n - \delta_1)^2$$

and the value of the first ionization energy, $E_{i,1}$, is adjusted until the quantum defect, δ_1, is fairly constant for all values of the integer principle quantum number, n. The value of $E_{i,1}$ so determined is then applied to other series of absorption bands to check that it produces a reasonably constant value of δ_1 for them. The individual types of Rydberg series so identified are labelled as s, p or d type based on the value of δ_1 and the number of series of a given type allowed by the symmetry of the molecule. For long series, maximum observed value of $n \approx 14$, the ionization energy is determined to high accuracy, ca. ± 5 cm^{-1}, provided that the individual band energies are accurately determined. We are particularly confident of the accuracy of the energies of the band maxima reported, having expended much effort on establishing a reliable calibration procedure for the spectrographic data and having tested it on a highly resolved spectrum, independently calibrated.[9]

Cyclohexanones

The absorption spectra of 2-, 3- and 4-methylcyclohexanone are shown in Fig. 1. Following the above prescription these are easily analysed in terms of Rydberg series of s-, p- and d-type as shown in Table 1. Most features are found to be single maxima, quite narrow in the case of the 4-methyl compound (about as narrow as the bands of the parent compound) but becoming progressively broader in the 3- and 2-methyl compounds. The $n = 3$ transitions of all the compounds exhibit extensive vibronic structure and there is clear evidence of such structure associated with higher n transitions of the 2-methyl compound. The absorption wavelengths listed in Table 1 correspond to the maxima of the origin absorption for any band.

Not surprisingly, the 4-methylcyclohexanone spectrum is very similar to that of cyclohexanone. Table 2 compares the observable length of, and the typical value of the quantum defect for, the various series in the set of molecules and shows that substitution at the 4-position has almost no discernible effect on the Rydberg structure. The spectrum shows
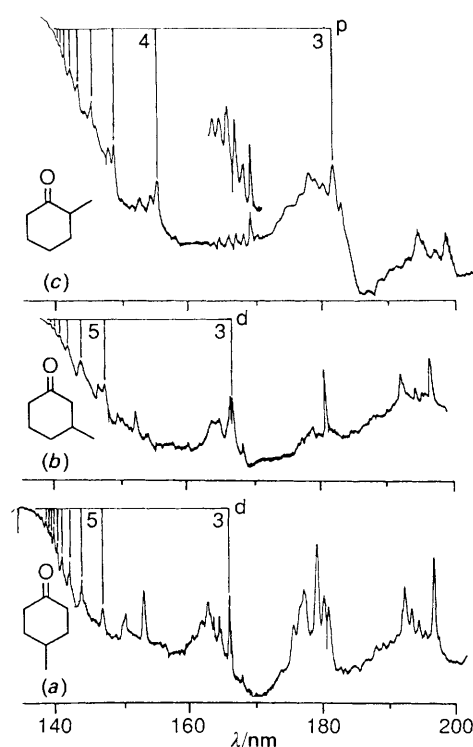

Fig. 1 Vacuum ultraviolet absorption spectra of (a) 2-methyl, (b) 3-methyl and (c) 4-methylcyclohexanone. The Rydberg assignments indicated correspond to Table 1

Table 1 Rydberg series of 4-, 3- and 2-methylcyclohexanone assigned using values of $E_{i,1}$ of 73 460, 73 416 and 73 465 cm^{-1}, respectively; each entry gives the absorption wavelength/nm and the quantum defect, δ_1, in parentheses

	4-methyl			3-methyl			2-methyl		
n	s	p	d	s	p	d	s	p	d
3	197.16 (0.80)	179.11 (0.51)	165.41 (0.10)	196.51 (0.79)	180.34 (0.53)	165.66 (0.10)	199.57 (0.82)	181.42 (0.55)	168.33 (0.21)
4		152.20 (0.24)					155.39 (0.53)		
5	149.37 (0.90)		145.68 (0.23)	1504.7 (1.03)	147.74 (0.73)	145.93 (0.26)		147.44 (0.59)	
6			142.55 (0.24)	145.93 (1.01)		142.54 (0.20)		143.36 (0.56)	
7			140.73 (0.24)			140.79 (0.22)		141.17 (0.54)	
8			139.58 (0.23)			139.56 (0.11)		139.89 (0.56)	
9			138.83 (0.24)			138.93 (0.27)		139.02 (0.54)	
10			138.29 (0.22)[a]			138.37 (0.21)		138.01 (0.56)	
11								137.68 (0.53)	

[a] 11, 137.90 (0.22); 12, 137.61 (0.22); 13, 137.38 (0.19); 14, 137.21 (0.23); 15, 137.07 (0.25); 16, 136.94 (0.12); 17, 136.83 (0.13).

Table 2 The ionization energies determined from the Rydberg assignments and the maximum value of the principle quantum number n and average quantum defect for the series observed, in parentheses
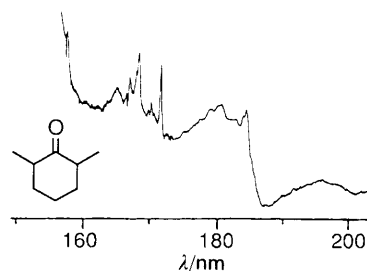
	E_i/cm^{-1}	$n_{max}(\langle \delta_l \rangle)$		
		s	p	d
cyclohexanone	73 795 ± 5	6 (0.82)	7 (0.52)	15 (0.24)
4-methyl-	73 460 ± 5	5 (0.85)	3 (0.50)	17 (0.22)
3-methyl-	73 416 ± 5	6 (1.00)	5 (0.65)	11 (0.26)
2-methyl-	73 465 ± 5	3	11 (0.45)	3
cyclopentanone	74 800 ± 5	8 (0.95)	5 (0.62)	14 (0.23)
3-methyl-	75 045 ± 10	7 (0.89)	8 (0.55)	8 (0.22)
2-methyl-	75 300 ± >10	5 (0.97)	5 (0.60)	4 (0.25)

Fig. 2 Vacuum ultraviolet absorption spectrum of 2,6-dimethyl-cyclohexanone

two distinct differences from that of the unsubstituted parent molecule,[2] in that E_i is 335 cm^{-1} lower in energy, an expected result of substitution, and there is no sensible Rydberg structure in the $n = 4$ region. Table 1 lists the only maximum observed in this region and it fits none of the series assigned. We are led to the only possible explanation that a major perturbing influence due to an iso-energetic molecular valence state is broadening the structure. In support of this we note that the corresponding bands of the parent molecule also show evidence of such an interaction. The 4s transition of cyclohexanone is anomalously weak and the 4p is the broadest band observed in the full spectrum of cyclohexanone. Other than this the spectrum of 4-methylcyclohexanone is similar to that of the parent being dominated by a long d-series which allows very accurate determination of the ionization potential. The similarity is not surprising considering the distance between the chromophore and substituent and encourages us in the belief that the $n = 4$ region is genuinely anomalous.

The other two cyclohexanones are found to have E_i very similar to 4-methylcyclohexanone but the spectra show progressive changes with the substituent position. The 3-methyl spectrum is basically similar to the 4-methyl and suffers the same problem with the $n = 4$ absorptions which, again, supports the proposed interference by a molecular state. The shorter length of the observable d-type transitions could be attributed to a more effective substituent–chromophore interaction, the internal pressure effect discussed above. This would not, however, account for the increased observability of the p-series, as this effect should affect all series, perhaps to differing extents but not to enhance one whilst reducing another. There is also evidence for some other process being operative in the quantum defects of the p- and s-series which are larger than those of the first two molecules.

When one considers the 2-methyl spectrum which is dominated by a long p-series and in which the d-series has become very short, and notes that the typical quantum defect value for this p-series is again distinctly different from the parent molecule but in the other direction, then an internal pressure effect has to be discarded as the source of the differences. If it had been active in the 3-methyl compound then it should be even more so in the 2-methyl, and no long series should be observable. We propose that the prime result of Rydberg orbital–substituent interaction in these molecules is a mixing of the orbitals of various atomic types with a consequent transfer of intensity from the d-series to the p-series.

The internal pressure effect of the substituent is expressed in these spectra in the general increase of bandwidth and the observation of vibronic structure at $n > 3$ mentioned above. It does not serve to suppress the Rydberg transition intensity as the mixing of orbitals of different atomic types allows one

(or more) of the resultant orbitals to be oriented along a direction that avoids the substituent. Introducing two methyl groups adjacent to the chromophore has the expected internal pressure result of broadening all Rydberg structure with $n > 3$ as is shown by the spectrum of 2,6-dimethylcyclohexanone in Fig. 2. The lowest energy transitions, involving as they do the smallest Rydberg orbitals, are least affected by the substituents and persist even in this crowded arrangement; but even so it is clear that only the 3d Rydberg orbital(s) is(are) able to avoid strong interaction with the methyl groups. No resolvable structure to higher energy than that shown in Fig. 2 is found.

Cyclopentanones

Fig. 3 shows the spectrographically recorded absorption spectra of 3- and 2-methylcyclopentanone. The absorption maxima are analysed in terms of Rydberg series in Table 3, and are compared with the parent molecule in Table 2. The changes compared to the parent found for the cyclohexanones are repeated here but in a rather less obvious manner. The cyclopentanone spectrum was dominated by a long d-series with only a weak, short p-series. In both the substituted molecules the d-, p- and s-series are of the same length and never achieve the length of the original d-series.
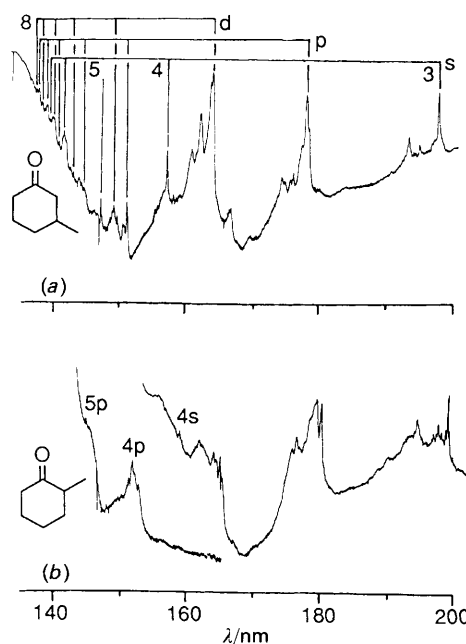
Fig. 3 Vacuum ultraviolet absorption spectra of (a) 3-methyl- and (b) 2-methyl-cyclopentanone. The Rydberg assignments indicated correspond to Table 3

Table 3   Rydberg series of 3-methyl and 2-methylcyclopentanone; series assigned using values of $E_{i,1}$ of 75 045 and 75 300 cm^{-1}, respectively; each entry gives the absorption wavelength/nm and the quantum defect in parentheses

	3-methyl			2-methyl		
n	s	p	d	s	p	d
3	198.69 (0.89)	178.24 (0.59)	163.92 (0.20)	201.17 (0.93)	180.58 (0.65)	165.51 (0.28)
4	155.93 (0.89)	150.72 (0.45)	148.73 (0.25)	159.25 (1.04)	151.96 (0.60)	147.94 (0.23)
5	146.64 (1.00)	143.95 (0.56)	142.34 (0.21)	145.89 (0.97)	143.11 (0.50)	
6	140.79 (0.77)	140.03 (0.50)	139.27 (0.18)			
7	138.67 (0.88)	138.23 (0.63)	137.50 (0.12)			
8		136.88 (0.57)	136.52 (0.18)			

Substitution is having a general effect in reducing the observable length of series (internal pressure) and a particular effect in moving intensity from the d- to the other series (orbital mixing). The general effect is responsible for the broadening of the individual bands compared to the parent, in fact the higher energy absorptions of 2-methylcyclopentanone appear as very weak features on the rapidly rising background in Fig. 3, but are quite clear in expanded spectra. Most obvious from Fig. 3 is that the p-series of 2-methylcyclohexanone carries the largest intensity and would be the dominant series if more transitions to higher energy were resolved. This is the same switch of intensity from d to p series as applied in 2-methylcyclohexanone.

The ionization energies of the substituted compounds are similar and larger than the parent, exactly the opposite effect to that found for the cyclohexanones and to that expected from the numerous studies on substitution effects on ionization energy. We can currently offer no explanation for this unexpected effect of substitution on the ionization energies.

Absolute Intensities

Table 4 gives the oscillator strengths measured for the $n = 3$ transitions of the compounds and an estimate of the total oscillator strength of all transitions to higher energy than these. In the unsubstituted molecules we were able to measure the values of the lowest energy transitions with good accuracy as the bands were well separated,[4] but an estimate of the underlying continuum had to be made for the higher energy bands. The continuum is now a complication with the low energy transitions as well, interfering increasingly with increasing degree of substitution. As a result we are less confident about the oscillator strengths of the substituted molecules in Table 4, even though the molar absorption coefficients are measured to the same degree of accuracy as they were for the parent molecules. Fig. 4 shows the photometrically recorded spectra of the cyclohexanones, the molar absorption coefficient values, and examples of the background level used in the calculation of the oscillator strengths. Fig. 4 demonstrates the extent to which the pho-

Table 4   Oscillator strengths of the $n = 3$ Rydberg transitions of the cyclic ketones and their methyl substituted derivatives, and an estimate of that of all Rydberg transitions with $n > 3$; all values $\times 10^{-2}$

	3s	3p	3d	$\sum n > 3$	total
cyclohexanone	1.18	2.3	1.5	5.9	10.9
2-methyl-	0.26	2.4	1.1	2.5	6.3
3-methyl-	1.13	1.1	3.0	2.0	7.2
4-methyl-	0.69	1.8	1.5	3.5	7.5
cyclopentanone	2.06	2.2	2.5	3.5	10.9
2-methyl-	0.65	1.6	1.2	2.2	5.7
3-methyl-	1.25	0.9	2.4	1.3	6.0
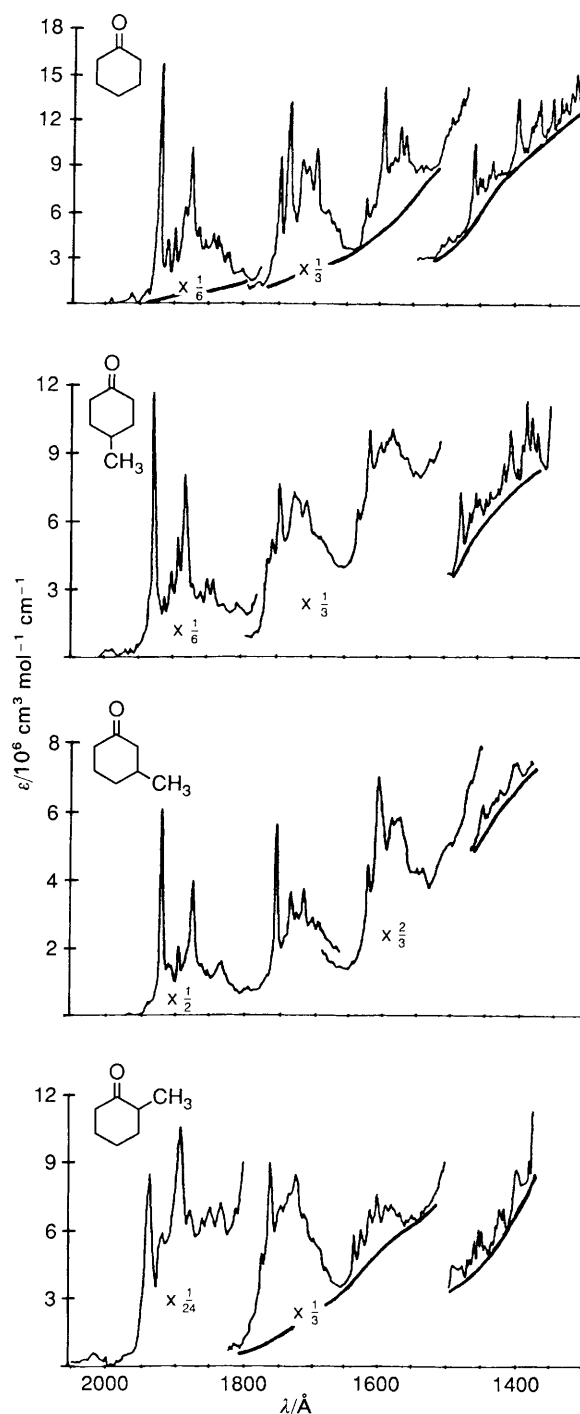
Fig. 4   Photometrically measured spectra of the cyclohexanones. The continuous line indicates the background level used in determining the oscillator strengths give in Table 4

tographic data of Fig. 2 misrepresents the true lineshape of the spectrum owing to the plates being an approximately logarithmic detector of transmitted intensity. They tend to make bands of very different absorbance appear to be of similar intensity. It also demonstrates the necessity of using high resolution for the spectra of even such large molecules. Much of the high energy structure of Fig. 4 is similar to the noise common in such spectra (a result of using the structured hydrogen discharge as the light source for this region, the normal light source for photometric measurements), and could only be identified certainly as Rydberg structure by comparison with the photographic data.

The most notable difference between the unsubstituted and substituted molecules from Table 4 is the drop in total oscillator strength. We believe this to be real, despite the uncertainties associated with the comments above, as it applies for 4-methylcyclohexanone which in all other respects is similar to the parent. Noting that this difference is progressive with the proximity of the substituent to the chromophore and also with decreasing ring size, we suggest that it reflects enhanced Rydberg–valence mixing induced by the substituent through the transfer of Rydberg transition intensity to the underlying continuum. This is another aspect of the general substituent, internal pressure, effect rather than of orbital mixing, and is one that we have not identified before although it probably applied to our data on substituted *para*-benzoquinones.[2] Otherwise there are no systematic trends for individual bands obvious from the data, which is so unlikely that we suspect that the interference of the continuum is masking the real variations.

Centre of Charge Calculations

We have accounted for the similarity and differences between the Rydberg spectra of a number of ketone compounds by considering the location of the origin of the set of Rydberg orbitals and the possible orientation of the orbitals with respect to molecular bonds and symmetry axes. The argument is that the optical electron in a large radius Rydberg orbital senses the charge of the cationic core as emanating from a point, and that this can be reasonably located at the centre of charge of the molecular cation. This point then constitutes the geometric origin of the set of Rydberg orbitals. If the molecule has an axis of symmetry, as in acetone or cyclopentanone, then this restricts the possible orientation of the orbitals (no matter that orbitals of different l type may be mixed). If the molecule has only a plane of symmetry, as in acetaldehyde or cyclohexanone, then there is free-choice of the orientation of the orbitals in the plane. They can be directed to avoid overlapping bonding regions, thereby avoiding predissociative interaction, and/or to overlap the initial n_0 orbital enhancing the transition intensity. This latter effect is possible as the n_0 orbital is fixed perpendicular to the carbonyl bond by bonding rather than symmetry considerations. (Obviously in the case of only C_2 axial symmetry the same free-choice exists in the orientation of the orbitals perpendicular to the rotation axis, but in the one case considered, cyclopentanone, there was no evidence for the orientation as the orbitals are necessarily directed away from n_0.)

We have previously calculated the centre of charge through *ab initio* molecular orbital methods. In this present work we have used the semi-empirical AMPAC calculation as the molecules are simply too large for convenient use of *ab initio* methods. The results from the two methods are very similar probably because, as we have commented before, the centre of charge is such a gross property, being an average over the full electron density of the ion, that it is not likely to be particularly sensitive to the level of approximation used. The

result of these calculations for the parent compounds is that the centre of charge is located along the carbonyl axis (slightly above it in cyclohexanone) and back inside the ring bisecting the β-carbons in cyclopentanone and 25 pm further back in cyclohexanone. The effect of the substituents on the position is very small. At most the centre of charge moves 30 pm towards the substituent, the largest movement being in 2-methylcyclopentanone. This is too small an effect to explain the spectroscopic variations observed and we are left only with the orientation of the orbital sets as the cause of the differences.
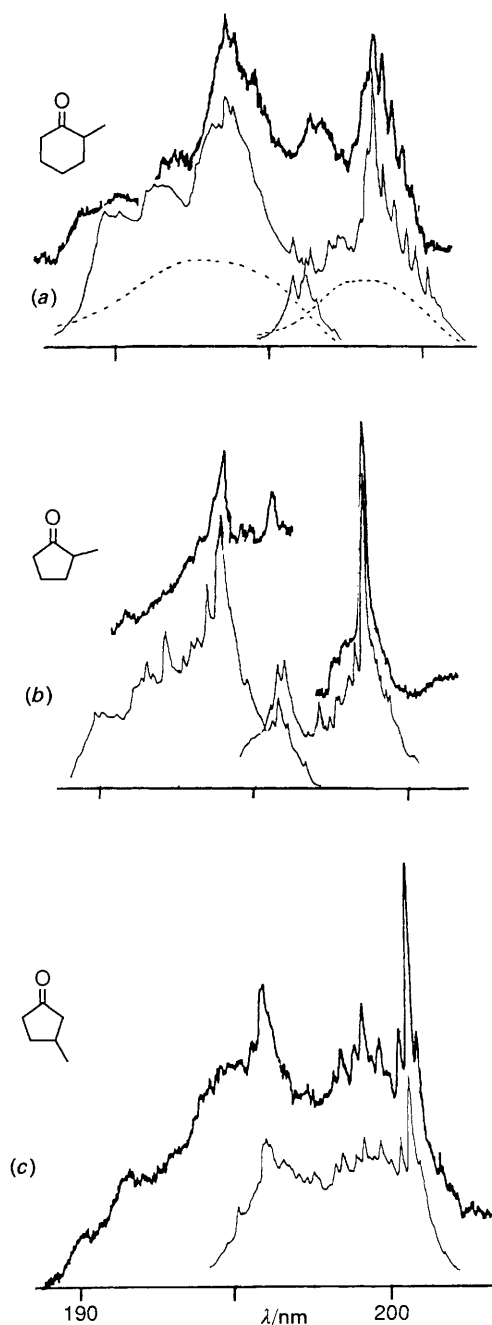
$n_0 \rightarrow 3s$ Transitions

These transitions are unlike any others in the spectrum as they show a quantity of vibronic structure. This has previously been studied by Cornish and Baer (CB) using high-resolution $(2 + 1)$REMPI spectra of samples cooled in a molecular jet and the vibronic features are very distinct.[5,6] Our data, being on room-temperature samples, cannot compete in quality with those results, however we find a number of features that are additional to the laser spectra by virtue of our samples being at room temperature which merit some discussion.

In order to compare thoroughly with the results of CB we have also measured the REMPI spectra of the samples but in a static cell system and, rather surprisingly we find that the absorption spectroscopic band shapes and the $(2 + 1)$REMPI ones are identical in the energies of features and differ, to only a small extent, in their intensities. Of course, given the low symmetry of the molecules, there are no selection rule differences between the two techniques, all transitions being allowed. Further, there are no electronic states at the one photon energy of the two photon absorption step of the REMPI to enhance the cross-section of one type of electronic transition over another. Even so, there is no fundamental reason why the two techniques should produce such similar band shapes. We find that all the major bands of the cooled spectra are present in both our measurements but, of course, not nearly so well resolved; in fact no discussion of the structure could have been contemplated without the earlier work.

Fig. 5 shows the absorption and static cell REMPI spectra of three of the compounds and the comparability of the measurements is obvious. Of greatest interest is the structure observed in the region of the origin of 2-methylcyclohexanone. We observe a series of six lines separated by 88, 86, 85, 81 and 80 cm^{-1}, culminating in the most intense line at 50 361 cm^{-1}; whilst CB report three lines separated by 85, 90 and 88 cm^{-1}, the lowest energy one being the origin at 50 171 cm^{-1}. The question is which of the six lines we observed at room temperature is the origin, and becomes a matter of the relative calibration of ours and CB's spectra. This can be decided by comparing other spectra in which there is no doubt about the location of the origin; 3-methylcyclohexanone, in which we find the origin to be 20 cm^{-1} higher in energy than CB, and 4-methylcyclohexanone, 10 cm^{-1} higher in energy. We are confident, therefore, that the origin of our 2-methyl spectrum is the line at 50 195 cm^{-1}, 24 cm^{-1} higher than CB. We are observing two quanta of the excited-state vibration, as do CB, and three hot bands due to the ground state mode. The vibrational mode involved is thought to be the ring-bending torsion between the chair and boat conformers of the six-membered ring[6] and we see that it has much the same energy in the ground and $(n_0, 3s)$ excited states, a not particularly surprising result but one not available from the cooled molecular spectra alone.

CB note that the spectrum of 2-methylcyclopentanone shows far less activity of the low-frequency mode, suggesting

Fig. 5 Photographically recorded absorption spectra and multiphoton ionization spectra of (a) 2-methylcyclohexanone, (b) 2-methylcyclopentanone and (c) 3-methylcyclopentanone showing the vibronic structure of the $n_0 \rightarrow$ 3s transition. The absorption spectrum is the upper line, and the wavelength shown is that of the absorption spectrum. The dotted line in (a) indicates the intensity variations of the dyes used in the REMPI experiment.

that this is due to less geometric reorganisation in the excited state. This observation is supported by our room-temperature data, Fig. 5(b), in which there is only one hot band to the red of the origin. A distinct difference is found, however, in the spectra of 3-methylcyclopentanone. CB find very little intensity in the vibronic features of the whole spectrum and almost none at low frequencies. In comparison, there is a quantity of structure in both our spectra, best resolved in the REMPI data. There are five resolved maxima all within 150 cm^{-1} to the red of the origin, and more to the blue. Similar structure

is associated with every intense feature in the spectrum. We suspect that all of this is due to sequence absorptions (no change of vibrational excitation) involving low-frequency modes, ring inversion and/or methyl rotation, which are completely lost on cooling the sample.

The most intense vibronic band to higher energy than the n_0, 3s) origin in all the photoabsorption spectra is found at very similar separations from the origins; for the cyclohexanones, 1184 cm^{-1} in 4-methyl, 1180 cm^{-1} in 3-methyl and 1192 cm^{-1} in 2-methyl, and for the cyclopentanones 1188 cm^{-1} in 3-methyl and 1228 cm^{-1} in 2-methyl. These are almost certainly the carbonyl-stretch frequencies of the excited states in each case, although the precise values are not certain as CB's spectra show that in each case there is more than one absorption in this region. Presumably owing to the problem of dye intensity variation, the absorptions in this region do not appear to be significantly more intense than the adjacent transitions in CB's spectra.

The biggest difference between CB's cooled molecular spectra and our data is found for the 2,6-methylcyclohexanone molecule. As shown in Fig. 2 the room-temperature absorption is a broad featureless band, whilst CB report a very well resolved, admittedly very complex, system of vibronic lines. Obviously we can add nothing to CB's comments on this spectrum, but the comparison shows that a sample handling system allowing absorption spectra of molecular beams should yield well resoved spectra, not only in the (n_0, 3s) region, but throughout the Rydberg region of the molecules. Such a system is under development. (In fact photometric versions of this experiment have already been reported[10] but are limited in the wavelength range they can cover, and have employed only medium-resolution monochromators. There is also some question that they can suffer an inherent resolution problem owing to the photometric detection method.[11])

Conclusions

The prime purpose of this work was to investigate the substituent effect on the Rydberg transition of ketone molecules. We have identified two distinct processes. First, the mixing of orbitals of different atomic type which results in distinct changes in the quantum defects of series and a shift of intensity from d to p type series. Secondly, a general broadening of absorption bands and a tendency for series to become unresolved at low values of n. The former is a new observation, and one obvious corollary is that the orbital arising from the mixing avoids interaction with the substituent. Why this orientation should be the most energetically favourable is not obvious and will require some computational method capable of treating high energy states of such large molecules for a full explanation.

The latter process is that which we have previously identified as an internal pressure effect. The general broadening of structure could be due to an increase in vibronic activity, but we consider the results of previous work on *para*-benzoquinones to justify our opinion. The REMPI study on the substituted cyclic ketones, quoted extensively above, may appear to cast doubt on this process, as the $n_0 \rightarrow$ 3s band of 2,6 dimethyl cyclohexanone shown in that work is a finely resolved vibronic system. We think that this is a particular feature of the lowest energy transition as it involves the smallest Rydberg orbital, the one least affected by the substituents. Thus we expect the broad structureless 3s band of Fig. 2 will sharpen to show structure similar to the REMPI, but that no higher energy Rydberg structure will be observed.

References

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