Electronic Excitations in Bicyclohexylidene

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A reinvestigation of the electronic excited states of the olefin bicyclohexylidene has been carried out using the techniques of photoelectron, electron impact, and multiphoton ionization spectroscopies. Our studies show that the multitude of sharp structures in the vapor spectrum (40 000–65 000 cm⁻¹) are due to Rydberg excitations originating at the π MO of the olefin chromophore. These excitations are near degenerate as a consequence of the extreme alkylation of the olefin and are separable only by combining photoelectron and threshold electron impact techniques. The anomalously high intensities of the overlapping Rydberg bands are due to two underlying valence excitations, whereas only one (π → π*) is expected. Two transitions also appear in the crystal spectrum in the same energy region and correlate with the underlying valence excitations of the vapor phase rather than with the more prominent Rydberg promotions; it is suggested that the second valence transition is due to a π(CH₂) → π* intramolecular charge transfer involving the cyclohexyl rings and the double bond. The two-photon selection rules evident in the multiphoton ionization spectrum of bicyclohexylidene point to C₂ᵥ symmetry in the vapor phase.

Introduction

In general, the parade of electronic excitations in the alkyl olefins below 8 eV is quite regular, with the pattern of π → 3s, π → 3p, and π → 3d Rydberg excitations interrupted only by the intrusion of the π → π* valence excitation in the vicinity of the transition to 3s.¹ Valence transitions between π and σ valence MO's occur at yet higher energies and rarely have been identified with any confidence.

The various Rydberg excitations in alkyl olefins have been identified as such on the basis of (a) the term values of the excitations (ionization potential minus the excitation energy), (b) the spectral response to external perturbation on going from the vapor phase to a condensed phase, and (c) their oscillator strengths.¹ Elaborating on the above points, the term values of Rydberg transitions terminating at 3s, 3p, and 3d Rydberg orbitals fall in the ranges 27 000–21 000, 21 000–18 000, and 14 000–11 000 cm⁻¹, respectively, with the variation within each range related directly to the number and bulk of the pendant alkyl groups. Note that in the limit of very large alkyl groups (10 or more carbon atoms per molecule), the term values of transitions terminating at 3s and 3p in olefins are nearly equal.

When studied in absorption, the Rydberg bands of a molecule's vapor-phase spectrum are so strongly perturbed on going into solution or into a solid phase¹ that they often are cited as "missing" in the condensed-phase spectra. Studies of this effect using the circular dichroism of chiral derivatives show that the Rydberg bands upon external perturbation are not "missing" but are broadened and shifted to higher frequencies.¹,² Lowering the temperature of such solutions further shifts the CD band centers to higher frequencies. In contrast, a valence excitation such as π → π* will be shifted to lower frequency upon entering the condensed phase, and lowering the temperature has no further effect on the transition frequency. As for the oscillator strength distinction between Rydberg and valence transitions in the alkyl

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(10) Clausen, B. S.; Christensen, P. H.; Morup, S., to be published.

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ELECTRON ENERGY LOSS, ev

Figure 2. Electron energy loss spectra of bicyclohexylidene at constant residual energy \( E_r \). The dashed curves are the \((\pi)\) photoelectron band envelopes (Figure 1, bottom), positioned so as to coincide with the Rydberg excitations originating at \( \pi \) MO.


Figure 1. He I photoelectron spectrum of bicyclohexylidene in the vapor phase (upper panel), and detail of the first band (lower panel).

Among alkyl-olefin spectra, that of bicyclohexylidene (BCH) is exceptional, for it seems not to follow the olefin spectral pattern discussed above. The absorption spectrum of BCH vapor shows two intense features, \( f = 0.19 \) and \( 0.26 \), centered at 48 000 and 55 000 cm\(^{-1}\). Though the sharp vibronic structures in these bands are much more suggestive of Rydberg excitations than of \( \pi \rightarrow \pi^* \) valence bands, their oscillator strengths are much more compatible with valence transitions, and furthermore, there is otherwise no discrete feature in the absorption spectrum which can be assigned as \( \pi \rightarrow \pi^* \). Moreover, the reflection spectrum of a single crystal of BCH shows distinct transitions centered at 48 000 and 51 000 cm\(^{-1}\), each of which has perfect long-axis polarization. By virtue of their appearance in the solid phase, it is clear that the two bands of the crystal are valence excitations. Snyder and Clark\(^5\) tentatively assigned these crystal transitions of BCH as \( \sigma \rightarrow \sigma^* \) and \( \pi \rightarrow \pi^* \), respectively, and correlated them with the two transitions at 48 000 and 55 000 cm\(^{-1}\) in the vapor spectrum. Needless to say, the assignment of a \( \sigma \rightarrow \sigma^* \) transition as the lowest in an alkyl olefin is unexpected. However, the important point is that there are two low-lying valence transitions in the crystal spectrum, both polarized along the double bond.

The sum total of these observations on the BCH spectrum leads to a picture which in almost every detail is at variance with that normally accepted for olefin absorption. As we now have more spectroscopic data on BCH in the vapor phase, we feel that a more detailed interpretation can be given for the vapor spectrum, though a convincing interpretation of the crystal spectrum remains a problem. The new data on BCH encompass photoelectron, multiphoton ionization, solution absorption, and electron-energy-loss spectra.

Photoelectron Spectrum

The photoelectron spectrum (PES) of BCH (Figure 1) is most useful in interpreting its excitation spectrum on two counts. First, it allows one to compute term values with respect to the \( K \) orbital ionization potential, and, second, the Franck-Condon envelope of the \((\pi) \) PES band is expected to resemble closely the corresponding envelopes of the \( \pi \rightarrow nR \) Rydberg bands in the optical spectra. The vibronically structured band at 8.137 eV (65 630 cm\(^{-1}\)) in the PES of BCH (Figure 1) is the \((\pi) \) ionization; the 1360-cm\(^{-1}\) progression evident in this band presumably corresponds to \( \pi \) stretching in the ionic state. The electron energy loss spectrum of BCH (vide infra) shows ground-state vibrational bands at 2880 cm\(^{-1}\) (C-H stretch) and 1350 cm\(^{-1}\) (C=C stretch). Since there are 12 ionizations in the 10–17-eV region of cyclohexane,\(^6\) it is safe to assume that there are many more PES bands in the 9–18-eV region of BCH than the 8 or so that are resolved in Figure 1. We note that the energy of the \((\pi) \) PES band of BCH is in no way unusual for a heavily alkylated olefin.

Energy-Loss Spectra

Energy-loss spectra of BCH were determined with a trochoidal electron impact spectrometer operated at constant residual energy, \( E_r \).\(^7\) Spectra determined in this way having \( E_r \) of 20 eV or larger are known to approximate closely the electric-dipole spectrum as recorded optically, whereas with \( E_r \) equal to 1 eV or less, the optical selection rules can be strongly violated. In this case, both spin-forbidden and orbitally forbidden excitations may appear with

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TABLE I: Term Values and Rydberg Assignments in the Spectrum of Bicyclohexylidene

<table>
<thead>
<tr>
<th>(0,0) energy, eV</th>
<th>term value, cm⁻¹</th>
<th>upper state assignment</th>
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</thead>
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<tr>
<td>5.396</td>
<td>20750</td>
<td>(π, 3e)</td>
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<tr>
<td>5.49</td>
<td>20000</td>
<td>(π, 3p)</td>
</tr>
<tr>
<td>5.54</td>
<td>19300</td>
<td>(π, 3p')</td>
</tr>
<tr>
<td>6.41</td>
<td>12570</td>
<td>(π, 3e)</td>
</tr>
<tr>
<td>6.67</td>
<td>10500</td>
<td>(π, 4e)</td>
</tr>
<tr>
<td>7.41 (°)</td>
<td>4500</td>
<td>(π, 5d) (°)</td>
</tr>
<tr>
<td>7.969</td>
<td>0</td>
<td>IP</td>
</tr>
</tbody>
</table>

*Measured with respect to the (0,0) band of the PES spectrum at 7.969 eV.

TABLE II: Comparison of MPI and Optical Spectra of BCH

<table>
<thead>
<tr>
<th></th>
<th>MPI one-photon</th>
<th>MPI two-photon</th>
<th>optical absorption</th>
</tr>
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<tbody>
<tr>
<td>wavelength, Å</td>
<td>resonance, eV</td>
<td>peaks, eV</td>
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<tr>
<td>4488</td>
<td>5.525</td>
<td>5.391</td>
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<tr>
<td>4347</td>
<td>5.700</td>
<td>5.577</td>
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<td>4210</td>
<td>5.89</td>
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<td>4055</td>
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<td>3870</td>
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<td>5.491</td>
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<td>6.252</td>
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Discussion

It is clear from the above analysis that the structured bands of BCH vapor in the 43 000-60 000-cm⁻¹ region are Rydberg excitations originating at the π MO. The term values observed for these bands are typical of those seen for chromophores at the alkyl limit. Because such Rydberg excitations do not persist in condensed phases, the structured bands of the 43 000-60 000-cm⁻¹ region of the vapor are not related to those of the crystal spectrum in the 43 000-55 000-cm⁻¹ region.

The absence of the π → 3s transition and the presence of the π → 3p band in the MPI spectrum at the two-photon level follows the selection rules appropriate to ethylene itself, suggesting that BCH in the vapor phase has C₆₅₈ symmetry as in the crystal. Because π → 3p is forbidden in the one-photon spectrum of the C₆₅₈ molecule, it is postulated that the appearance of this band in the optical spectrum is induced by odd quanta of C=C torsion. The low-frequency allowing mode is expressed as the difference of optical and MPI origin frequencies but our resolution does not allow an accurate measurement of this. In support of this scenario, we note that the variation of energy loss in the π → 3p region with Eₜ is strongly suggestive of dipole-forbidden excitations.

This interpretation of the new spectral data on BCH leads to a picture which parallels that for other alkyl olefins up to a point. There is nothing outwardly unusual about the π±σ* manifold in this molecule in the vapor phase, but the Rydberg structure is complicated by the fact that the π → 3p manifold is split into two poorly resolved transitions which in turn are nearly degenerate with π → 3s. Once shorn of its Rydberg bands, the spectrum of BCH in pentane solution shows two low-lying valence bands, which presumably are responsible for the high molar extinction coefficients observed for the 48 000- and 55 000-cm⁻¹ peaks of the vapor-phase spectrum. These peaks seemingly correlate with those of the crystal in the same spectra region; however, the apparent vibronic structures of the crystal transitions are strangely missing from the vapor and solution spectra. The clear presence of two intense valence excitations in the region of the lowest Rydberg states reveal Rydberg resonance states but not valence resonance states. Moreover, if the symmetry of the molecule is high, then the appearance and/or nonappearance of transitions in the one-photon and two-photon spectra relate directly to the symmetries of the excited states. The MPI spectrum of BCH vapor in the one-photon wavelength range 5000-3580 Å (20000-27 900 cm⁻¹) reveals resonance peaks as recorded in Table II; beyond a two-photon energy of 6.5 eV (52 400 cm⁻¹), the MPI spectrum is intense but structureless. Comparison of the MPI peak energies as two-photon resonances with the one-photon absorption peaks, Table II, shows several apparent coincidences. However, the excitation to 3s with a one-photon origin at 5.391 eV (43 480 cm⁻¹) is not seen in the MPI spectrum even though it is energetically feasible as a (2 + 1) transition.

Multiphoton Ionization Spectra

The MPI spectrum of BCH is relevant to the question of assignments in the optical and energy-loss spectra, for the MPI spectra reveal Rydberg resonance states but not valence resonance states. Moreover, if the symmetry of the molecule is high, then the appearance and/or nonappearance of transitions in the optical and two-photon spectra relate directly to the symmetries of the excited states. The MPI spectrum of BCH vapor in the one-photon wavelength range 5000-3580 Å (20000-27 900 cm⁻¹) reveals resonance peaks as recorded in Table II; beyond a two-photon energy of 6.5 eV (52 400 cm⁻¹), the MPI spectrum is intense but structureless. Comparison of the MPI peak energies as two-photon resonances with the one-photon absorption peaks, Table II, shows several apparent coincidences. However, the excitation to 3s with a one-photon origin at 5.391 eV (43 480 cm⁻¹) is not seen in the MPI spectrum even though it is energetically feasible as a (2 + 1) transition.

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References

spectra of alkyl olefins are more complicated than previously acknowledged, though the complications may be evident only in certain highly alkylated systems.

One tempting clue as to the identity of the second valence excitation in BCH comes from the photoelectron work of Heilbronner et al. on the "ribbon orbitals" of species containing the cyclohexane ring. The orbitals in question are related to the highest-filled MOs of cyclohexane (4e,64) and are composed of π(CH3) and σ(σCC) local orbitals. According to the photoelectron study, the ribbon MOs are separated from the tangle of the other π, σ MOs by an appreciable gap in containing the cyclohexyl group. The ribbon MOs of BCH are observed at 9.8 eV in the photoelectron spectrum of Figure 1. As a result of their lower ionization potential, the ribbon orbitals "are good donor orbitals and ... they must play an important, if not dominant role in intramolecular charge transfer processes".15 Extension of this idea leads directly to the assignment of the two low-lying valence transitions of BCH as π → π* and π(CH3) → π*, the latter being largely an intramolecular charge-transfer transition from the cyclohexyl group to the double bond. Both of these transitions are allowed with long-axis polarization.

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**Shock-Tube Study of the Rate Constant for Excited OH* (2Σ+) Formation in the N2O–H2 Reaction**

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The OH* 2Σ+→I emission is known to occur in N2O–H2, highly diluted with Ar, as shown in Figure 1. The rate of OH* formation from OH* and N2O is given below.

\[ \text{OH}^* + \text{N}_2\text{O} \rightarrow \text{OH}^* + \text{N}_2 \]

The OH* formation was observed by using a Hamamatsu R-306 photomultiplier after passing through an interference filter (λmax = 3055 Å, half-width = 150 Å) located behind a quartz window of the shock tube and through two slits either 0.18 and 0.24 mm wide separated by a cylindrical tube 2 cm long. The ultraviolet and infrared emissions were observed simultaneously behind reflected shock waves. The OH* concentration was determined from the OH* emission intensity by using the relationship between OH* concentration and voltage found before. Data interpretation was carried out by computer simulations essentially as described previously.

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*Advanced Instrumentation Center for Chemical Analysis.

†Department of Chemistry.

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