Theoret. chim. Acta (Berl.) 21, 309—322 (1971)

Commentationes

Electronic Transitions in Mono-Olefinic Hydrocarbons

Part II. Experimental Results*

F. H. WATSON, JR.** and S. P. MCGLYNN

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803

Received June 11, 1970

Investigation of the onset of absorption in the spectra of liquid mono-olefins reveals transitions which seem too intense to be of a triplet ← singlet nature. Comparison with calculated intensities and excitation energies suggests that an $R^* \leftarrow N(\pi \rightarrow \sigma^*)$ assignment migth be appropriate.

The $R(3s) \leftarrow N$ transitions in the vapor spectra have been re-investigated and f-numbers have been estimated. Comparison with calculated intensities indicates that this transition might gain part of its intensity *via* vibronic stealing from the $V \leftarrow N$ transition. This mechanism is shown to offer a possible – but by no means unique – explanation for the vibrational structure of the $R(3s) \leftarrow N$ transition of cyclopentene.

Self-pressure dependence of the $R(3s) \leftarrow N$ transition in mono-olefins indicates, as do MO calculations, that the 3*s* Rydberg orbital is neither as diffuse nor as atomic-like as it is usually assumed to be in these molecules.

Die Untersuchung des Absorptionsbeginns in den Spektren flüssiger Monoolefine zeigt Übergänge, die zu intensiv erscheinen, um vom Triplet-Singlet-Typ zu sein. Der Vergleich mit berechneten Intensitäten und Anregungsenergien läßt vermuten, daß eine Zuordnung $R^* \leftarrow N(\pi \rightarrow \sigma^*)$ richtig sein könnte.

Die $R(3s) \leftarrow N$-Übergänge in der Dampfphase wurden untersucht und die f-Werte abgeschätzt. Der Vergleich mit berechneten Intensitäten zeigt, daß dieser Übergang ein Teil seiner Intensität über vibronische Wehcselwirkung vom $V \leftarrow N$-Übergang gewinnen könnte. Es wird gezeigt, daß dieser Mechanismus eine mögliche – aber keineswegs eindeutige Erklärung für die Schwingungsstruktur des $R(3s) \leftarrow N$-Übergangs von Cyclopenten darstellt.

Die Abhängigkeit des $R(3s) \leftarrow N$-Übergangs vom Eigendruck in Monoolefinen zeigt, ebenso wie MO-Rechnungen, daß das 3*s*-Rydberg-Orbital weder so diffus noch so atomartig ist, wie es normalerweise in diesen Moelkülen angenommen wird.

L'étude de l'absorption dans les spectres des mono-oléfines liquides révèle des transitions qui semblent trop intêses pour être du type triplet ← singulet. La comparaison avec les intensités et les énergies calculées suggère une identification du type $R^* \leftarrow N(\pi \rightarrow \sigma^*)$.

Les transitions $R(3s) \leftarrow N$ dans le spectre en phase vapeur ont été réétudiées et l'on a évalué les nombres f. La comparaison avec les intensités calculées indique que cette transition acquiert une partie de son intensité par couplage vibronique à partir de la transition $V \leftarrow N$. Ce mécanisme offre une explication possible – mais certainement pas unique – pour la structure vibrationnelle de la transition $R(3s) \leftarrow N$ du cyclopentene.

La dépendance à la pression propre de la transition $R(3s) \leftarrow N$ dans les mono-oléfines indique, comme d'ailleurs les calculs O.M., que l'orbitale Rydberg 3*s* n'est ni aussi diffuse ni aussi atomique qu'on le suppose d'habitude dans ces molécules.

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* Supported by the United States Air Force and The United States Atomic Energy Commission —Biology Branch *via* Grants to the Louisiana State University.

** Present address: Biophysics Department, Michigan State University, East Lansing, Michigan 48823.

Introduction

In a prior work [1], we presented results of semiempirical calculations on mono-olefinic hydrocarbons. The computations indicated that the weak, initial absorption observed in liquid olefins in the region 4–5 eV ($f \sim 10^{-5}$) might be due to a transition which is $R^* \leftarrow N(\pi \rightarrow \sigma^*)$ in nature. This absorption is usually assigned as $T \leftarrow N$ or $T_R \leftarrow N$ where T is the ${}^3\Gamma_{\pi\pi^*}$ state and T_R is the ${}^3\Gamma_{\pi 3s}$ Rydberg state; however, it appears too intense [1] to be of triplet ← singlet nature. We have investigated the onset of absorption in several olefinic liquids to see if excitation energies and intensities are more consistent with a triplet ← singlet assignment, or with the $R^* \leftarrow N$ assignment. We tend to validate the $R^* \leftarrow N$ designation.

The previous calculations [1] confirm the transition observed in the vapor absorption spectra in the range $5 \rightarrow 6.5$ eV ($f \sim 10^{-2}$) as $R(3s) \leftarrow N$. We have reinvestigated the vapor absorption spectra in order to better determine intensities and f-numbers and to consolidate the comparison with quantum chemical computations. On the basis of intensity calculations, we had previously proposed [1] that this Rydberg transition gains part of its intensity *via* vibronic stealing from the $V \leftarrow N$ transition. We shall discuss this mechanism further with particular reference to the vibrational structure in the $R(3s) \leftarrow N$ transition of cyclopentene.

In general, computations showed [1] that the 3s atomic orbital can mix appreciably, in both bonding and antibonding combinations, with valence-shell orbitals. This would indicate that the Rydberg orbital is neither as diffuse nor as atomic-like as is usually assumed. In view of this, we have investigated the effect of self-pressure variations on both the $R(3s) \leftarrow N$ and $V \leftarrow N$ transitions at low pressures (0.1 to 100 mm). The results indicate that both transitions are very similar in their sensitivity to environment effects and that the upper excited states of both excitations possess roughly comparable valence-orbital and/or virtual-orbital characteristics.

Experimental

The olefins used were from Phillips Petroleum Company — except tetramethylethylene which was from Aldrich Chemical Company. The purity specifications are:

Ethylene — 99.95 mole percent: determined by mass spectrometry. Most probable impurities are ethane and methane.

Propylene — 99.99 mole percent: determined by mass spectrometry. Most probable impurity is propane.

Isobutene — 99.95 mole percent: determined by GLC. Most probable impurity is butene-1.

Cis-Butene-2 — 99.94 mole percent: determined by GLC and freezing point measurements. Most probable impurities are trans-butene-2 and 1,3-butadiene.

Trans-Butene-2 — 99.63 mole percent: determined by GLC, freezing point measurements and infrared spectrum. Most probable impurity is butene-1 with a trace of n-butane.

Trimethylethylene — 99.86 mole percent. No impurities determinable by GLC analysis. Most probable impurities are cis-pentene-2, trans-pentene-2 and 2-methylbutene-2.

Tetramethylethylene — No purity specifications were available other than the designation "puriss" which Aldrich quotes as "99.9 (plus) % pure".

Cyclohexane — 99.94 mole percent: determined by GLC. Most probable impurity is cyclohexane.

Cyclopentene — 99.99 mole percent: determined by GLC. Most probable impurity is cyclopentane.

The vapor spectra of the methyl-substituted olefins, ethylene, cyclopentene and cyclohexene were obtained on a Cary Model-15 spectrophotometer. A vacuum line for easy sampling and degassing was constructed at the instrument. Pressures above 1 mm were measured with a "Speedivac" torr gauge (Edward's High Vacuum, Ltd.). Pressures below 1 mm were measured using a Veeco Model DV-1M thermocouple gauge and a RG-31X gauge control which had been calibrated against a Vacustat McLeod gauge (Edward's High Vacuum Ltd.). The sample cell was part of the vacuum system and could be isolated at any desired constant vapor pressure of the olefin being studied. Cells were available in pathelengths of 0.1, 1, 10 and 100 mm and were constructed with far U.V. "ultrasil" windows.

The liquid olefin spectra were obtained on the Cary 15. The isomeric butenes were collected in the sample cell at dry-ice temperatures and were maintained as liquids by flowing cooled N_2 vapor through a specially constructed cell jacket.

Absorption Spectra of Liquid Olefins; the $R^* \leftarrow N$ Transition

Fig. 1 shows the initial absorption in various liquid olefins in the range 29.000 to 48,000 cm^{-1}. The spectra of tetramethylethylene, trimethylethylene, cyclopentene, and cyclohexene were obtained at room temperature. The isomeric butenes were collected as liquids at dry-ice temperatures and were maintained as liquids in the cells at temperatures below room temperature. Tetramethylethylene exhibits a band with three structured peaks at about 34,000 cm^{-1} with an extinction coefficient of 0.8. No such peak is apparent in either trimethylethylene or *trans*-butene-2. However, isobutene and cis-butene-2 show definite shoulders at $\sim$45,000 cm^{-1}; both of these shoulders have extinctions of $\sim$1 and are located in a region where the intensity is rising toward higher-energy excitations. Cyclopentene shows a shoulder at $\sim$40,000 cm^{-1} with a molar extinction of about 1. Cyclohexene shows a definite peak at 39,000 cm^{-1} with a molar extinction of $\sim$2.

These peaks may well be an $R^* \leftarrow N$(or $\pi \rightarrow \sigma^*$) transition. The intensity is weaker in tetramethylethylene than in either isobutene or cis-butene-2, as computations predict. The transition is not observed in trans-butene-2, as predicted by the calculations ($f_{\mathrm{calc.}} = 10^{-7}$). Because of the diffuse underlying absorption ($\varepsilon = 10^{-2} - 10^{-1}$), we could only estimate f-values. These experimental oscillator strengths are given in Table 1. They are several orders of magnitude larger than computed f-numbers for either the $T \leftarrow N$ or $T_R \leftarrow N$ transitions [1]. Table 1 shows a comparison between calculated and experimental $R^* \leftarrow N$ excitation energies and oscillator strengths. The agreement, from the point of view of energies, is quite good. The agreement of computed and experimental oacillator strengths is poor but within acceptable limits in view of the difficulties inherent in both the experimental and computational approaches used here. We offer no explanation

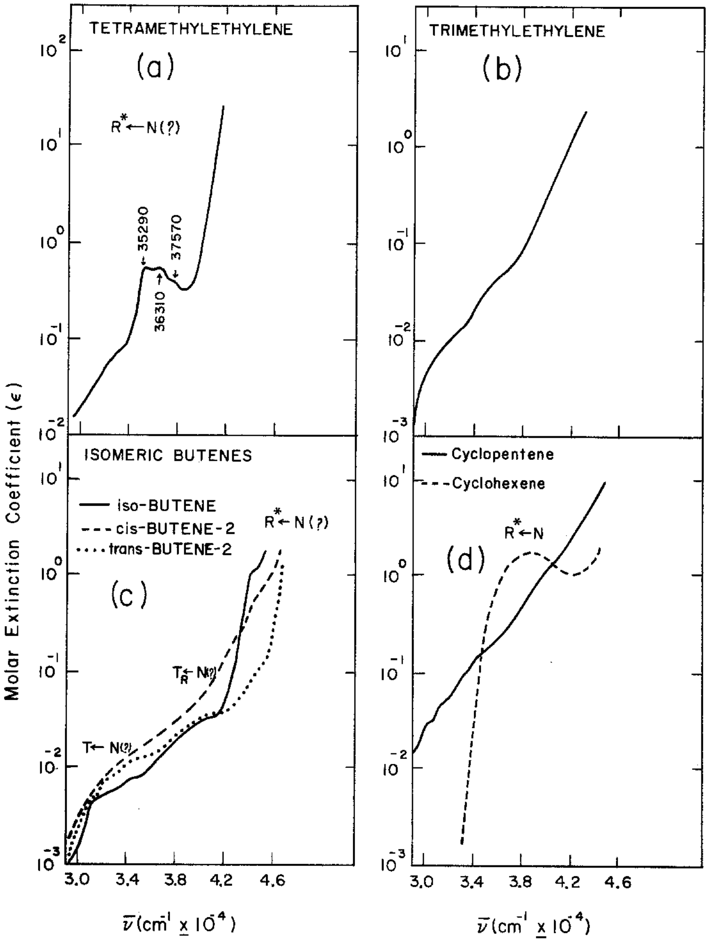


Fig. 1. Absorption spectra of liquid olefins

for the failure to observe the peak in trimethylethylene. It should, according to computations, occur at 33,700 cm^{-1}.

We feel rather confident that the reported absorption peaks are real and not the result of impurity absorptions. The purity specifications indicate that all likely contaminants are other mono-olefins which have no strong absorption peaks in this region. Even aromatics or conjugated hydrocarbons could not cause an extinction of 1 if present in the specified low concentrations. Thus, it is possible that we have located experimentally the $R^* \leftarrow N$ transition (actually $\pi \rightarrow \sigma^*$ in most cases) predicted by prior MO calculations [1].

Absorption Spectra of Liquid Olefins; the $T \leftarrow N$ and $T_R \leftarrow N$ Transitions

In each molecule, the underlying absorption ($\varepsilon = 10^{-2} - 10^{-1}$) might be due to $T \leftarrow N$ and $T_R \leftarrow N$ transitions. Assuming the peaks to be as wide as their corresponding singlet-singlet transitions, the estimated f-values are $\sim 10^{-7}$. These

Table 1. *Calculated and experimental quantities for an assumed $R^* \leftarrow N(\pi\rightarrow\sigma^*)$ absorption band*

Molecule	E (calculated) ($\text{cm}^{-1}\times 10^{-4}$) ($\zeta_{3s}=0.483$)	f (calculated) ($\zeta_{3s}=0.483$)	E (experimental) ($\text{cm}^{-1}\times 10^{-4}$)	f (experimental)
Ethylene	5.50	3.36×10^{-9}	6.0[a]	—[b]
Propylene	4.72	3.07×10^{-3}	—[c]	—[c]
Iso-Butene	4.49	1.36×10^{-3}	4.4	2.4×10^{-5}
Cis-Butene-2	4.50	4.06×10^{-3}	4.5	1.7×10^{-5}
Trans-Butene-2	3.49	1.06×10^{-7}	not observed[d]	—
Trimethylethylene	3.37	5.14×10^{-4}	not observed[e]	—
Tetramethylethylene	2.74	6.09×10^{-4}[f]	3.4	1.8×10^{-5}
Cyclopentene	3.48	—[c]	4.0	9×10^{-5}
Cyclohexene	—[c]	—[c]	3.9	$>10^{-5}$

[a] Observed at 7.45 eV in the electron impact spectrum of ethylene and assigned as an excitation to a g-state by Ross and Lassetre [2]. Assigned as either ${}^1B_{2g}\leftarrow{}^1A_{1g}(b_{3u}\rightarrow b_{1u})$ or ${}^1B_{1g}\leftarrow{}^1A_{1g}(b_{3u}\rightarrow b_{2u})$ by Merer and Mulliken [3]. Our assignment is ${}^1B_{2g}\leftarrow{}^1A_{1g}(b_{3u}\rightarrow b_{1u})$.

[b] Not observed in absorption spectroscopy.

[c] Not computed or not investigated.

[d] See Fig. 1 (C); if it does exist, it would appear to lie at energies greater than 4.4 eV.

[e] See Fig. 1 (B); if it does exist, it would appear to lie at energies greater than 4.2 eV.

[f] This transition is forbidden in a primitive D_{2h} symmetry. However, the intensity is quite dependent on the relative orientation of methyl groups. The number we quote here for f(calculated) is somewhat representative of random methyl group orientations.

values agree well with prior spin-orbit coupling computations [1]. In Fig. 1 (C), the spectra of the butenes show what appear to be two weak transitions at about 34,000 and 40,000 cm^{-1}. These are *tentatively* assigned as $T\leftarrow N$ and $T_R\leftarrow N$, respectively.

This assignment of the $T\leftarrow N$ band agrees with recent data of Mulliken and Itoh [4]. These authors located the $T\leftarrow N$ bands of propylene, isobutene and trans-butene-2 using the technique of oxygen enhancement and those of trimethylethylene and tetramethylethylene using the external heavy-atom perturbation technique. A correspondence of experiment and computation concerning the $T\leftarrow N$ transition is given in Table 2. The agreement of both sets of numbers is good.

Table 2. *$T\leftarrow N$ transition energy of ethylene and methyl-substituted ethylenes* ($\text{cm}^{-1}\times 10^{-4}$)

Molecule	E (calculated)[a]	E (experimental)
Ethylene	3.50	3.70[b]
Propylene	3.47	3.39[c, d]
Iso-Butene	3.44	3.30[c, d]
Cis-Butene-2	3.44	—
Trans-Butene-2	3.44	3.28[c, d]
Trimethylethylene	3.41	2.985[c, e]
Tetramethylethylene	3.41	2.94[c, e]

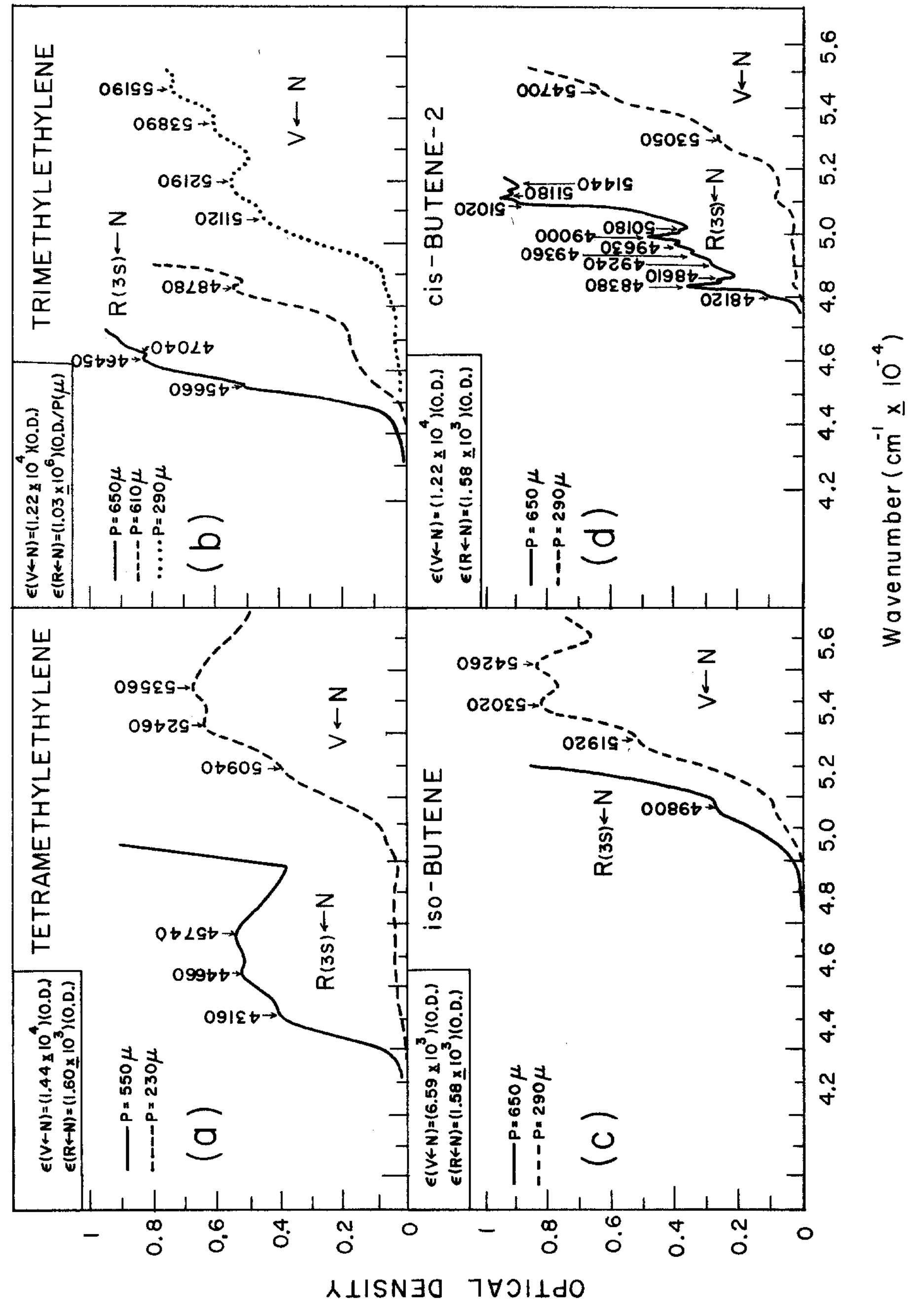
[a] See Table 11, Part I (Ref. [1] of text).

[b] See Ref. [5] of text.

[c] See Ref. [4] of text.

[d] Observed using technique of oxygen enhancement.

[e] Observed for solutions in CH_2Br_2.


TETRAMETHYLETHYLENE
(a)
ε(V←N)=(1.44 ± 10^4)(O.D.)
ε(R←N)=(1.60 ± 10^3)(O.D.)
—— P = 550μ
- - - P = 230μ
43160
44660
45740
50940
52460
53560
R(3S)←N
V←N
TRIMETHYLETHYLENE
(b)
ε(V←N)=(1.22 ± 10^4)(O.D.)
ε(R←N)=(1.03 x 10^6)(O.D./P(μ))
—— P = 650μ
- - - P = 610μ
····· P = 290μ
45660
46450
47040
48780
51120
52190
53890
55190
R(3S)←N
V←N
iso-BUTENE
(c)
ε(V←N)=(6.59 ± 10^3)(O.D.)
ε(R←N)=(1.58 ± 10^3)(O.D.)
—— P = 650μ
- - - P = 290μ
49800
51920
53020
54260
R(3S)←N
V←N
cis-BUTENE-2
(d)
ε(V←N)=(1.22 ± 10^4)(O.D.)
ε(R←N)=(1.58 ± 10^3)(O.D.)
—— P = 650μ
- - - P = 290μ
48120
48380
48610
49240
49360
49630
49000
50180
51020
51180
51440
53050
54700
R(3S)←N
V←N
OPTICAL DENSITY
0
0.2
0.4
0.6
0.8
1
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
Wavenumber (cm^-1 × 10^-4)

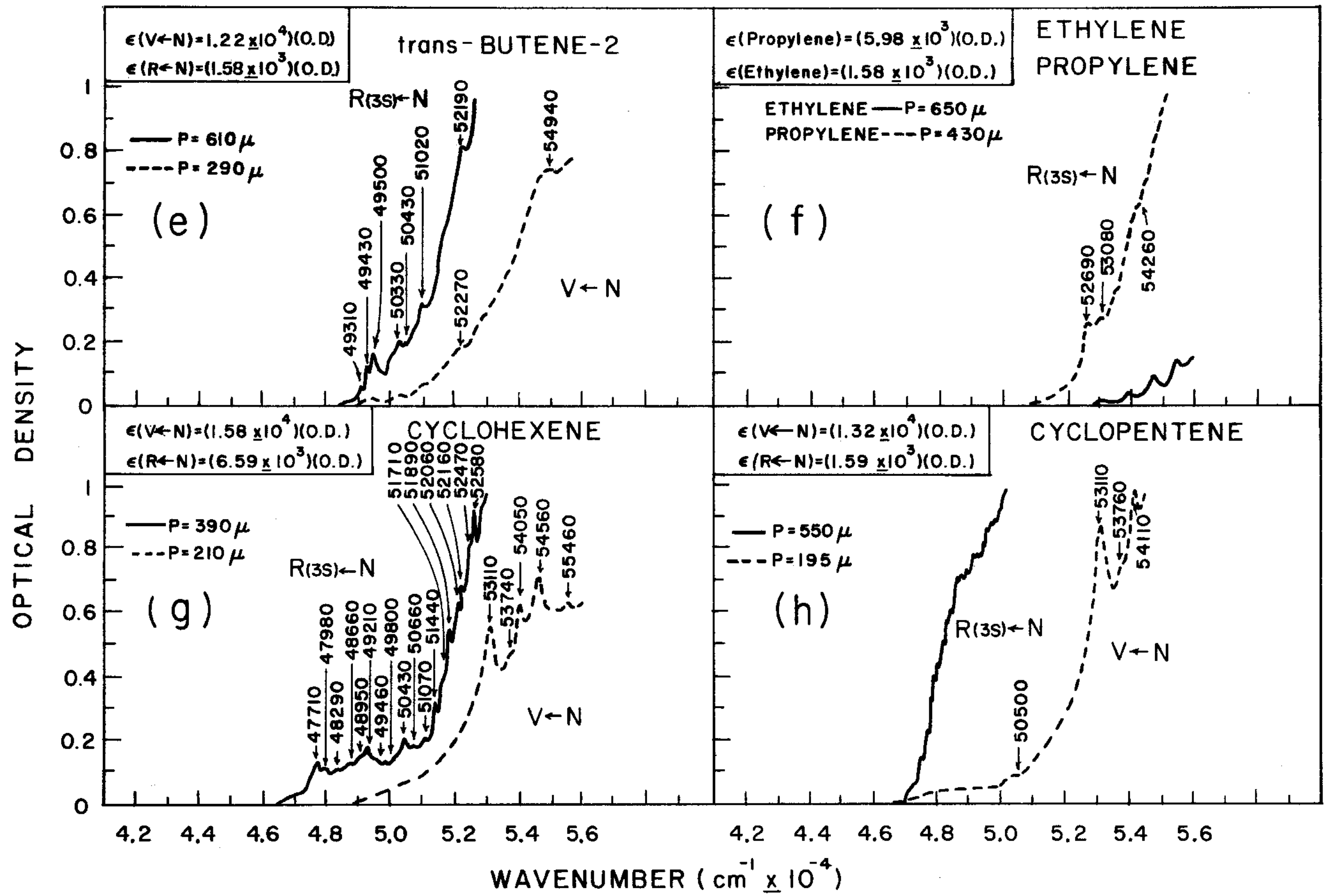


Fig. 2. Olefin vapor spectra. The ordinate is in optical density units; these units are convertible to molar extinction coefficients using equations presented in the upper left hand corners of the corresponding figures. The pressures at which the spectra were recorded are also indicated. The abbreviation for optical density is O.D.

Vapor Spectra and Pressure Dependence of the $R(3s)\leftarrow N$ Transition

The vapor spectra in Fig. 2 are all plotted in the same frequency range so that the shifts on decreased methylation may be easily seen. These data agree well with previously reported spectra, where available; the observed energy shifts also agree well with those computed [1]. The structure is very diffuse in most cases and vibrational analysis is not feasible. The spacings between main peaks are 1000 to 1500 cm^{-1} and are usually assigned to C = C stretching frequencies.

The extinction coefficients of olefinic transitions are functions of gas pressure. Such self-pressure studies have been carried out for both tetramethyl-ethylene and trimethylethylene in the pressure range 80 microns to 100 mm Hg and extinction coefficients have been evaluated on the basis of an assumed ideal gas behavior. The general behavior observed is noted in Table 3: The intensity of both transitions ($V\leftarrow N$ and $R\leftarrow N$) increases with increasing pressure, maximizes, and then decreases with continuing pressure increase.

That the self-pressure effects are not due to measurement error is evidenced by the fact that the $V\leftarrow N$ transition is effected more by increasing self-pressure than is the $R\leftarrow N$ transition. In addition, the maximum extinction coefficients occur at different pressures for the two transitions. We had expected the $R\leftarrow N$ transition to be much more sensitive to pressure variations than the $V\leftarrow N$ transition: We had reasoned that the 3*s*-A0 was large and diffuse and more open to environmental influences. Since it is not, at least at the low pressures used by us, it is implied that the *R* state contains more valence-shell character than is usually assumed. In other words, it is not appropriate to characterize the *R* state as a solely "big-orbit" state on the *V* state as a solely "non big-orbit" state.

Fig. 2 presents formulae for converting optical density to molar extinction coefficient. These formulae, are in every case, normalized to the average conversion factor observed in tetramethylethylene and trimethylene. By assuming that the Rydberg bands are the same width in all the olefins as in tetramethylethylene, we

Table 3. *Self-pressure effects on absorption intensity in trimethylethylene vapor*

Transition	$\varepsilon_{\max}$	Conditions
$V\leftarrow N$	2.85×10^3	$p = 160$ microns; thermocouple gauge; 10 cm cell
	3.69×10^3	$p = 290$ microns; thermocouple gauge; 10 cm cell
	4.49×10^3	$p = 390$ microns; thermocouple gauge; 10 cm cell
	1.45×10^4	$p = 1$ mm; torr gauge; 1 cm cell
	1.24×10^4	$p = 2$ mm; torr gauge; 1 cm cell
	6.81×10^3	$p = 20$ mm; torr gauge; 0.1 cm cell
	$(7.52 \pm 3.98) \times 10^3$	Average value
$R(3s)\leftarrow N$	5.68×10^2	$p = 390$ microns; thermocouple gauge; 10 cm cell
	9.19×10^2	$p = 550$ microns; thermocouple gauge; 10 cm cell
	1.68×10^3	$p = 610$ microns; thermocouple gauge; 10 cm cell
	8.47×10^2	$p = 6$ mm; torr gauge; 1 cm cell
	8.05×10^2	$p = 12$ mm; torr gauge; 1 cm cell
	7.70×10^2	$p = 100$ mm; torr gauge; 0.1 cm cell
	$(9.32 \pm 2.50) \times 10^2$	Average value

have estimated the experimental oscillator strengths previously reported [1] (Table 9 of Part I).

Figs. 2g and 2h show the vapor absorptions of cyclohexene and cyclopentene. The structure and position of the $R \leftarrow N$ transition in cyclohexene is remarkably similar to that of *cis*-butene-2. The main spacing is usually attributed to a $C=C$ stretching vibration. Cyclohexene thus appears to exhibit the typical spectral characteristics of olefins. However, the $R \leftarrow N$ transition of cyclopentene appears to differ from that of all other olefins: The dominant spacing is $\sim 130\ \mathrm{cm}^{-1}$. The usual assignment of this $130\ \mathrm{cm}^{-1}$ interval is either ring-puckering (ν_p) or, possibly, torsional-ring (ν_T) vibrations. No explanation has been offered as to why totally symmetric vibrations do not appear in this supposedly-allowed transition.

The ν_T vibration is essentially a torsion about the double bond; it is observed at $386\ \mathrm{cm}^{-1}$ in Raman spectrum [6]. Such a vibrational frequency should decrease greatly on going to an excited R state and the observed spacing of $130\ \mathrm{cm}^{-1}$ is not unreasonable for such a mode. The ν_p vibration is a puckering of the cyclopentene ring and has been shown by Laane and Lord [7] to have strongly anharmonic energy levels in the ground state. Such a vibration should not be extensively affected by electronic excitation and probably corresponds to the spacing observed in the excited R state.

Vibrational Analysis of the $R(3s) \leftarrow N$ Transition in Cyclopentene

The $R \leftarrow N$ absorption spectrum of cyclopentene is shown in Fig. 3 on an expanded frequency scale. The observed peaks agree well with those reported by Carr and Stücklen [8] with the following additional features: The peak they report at $48{,}490\ \mathrm{cm}^{-1}$ appears as a resolved doublet, 48,443 and $48{,}497\ \mathrm{cm}^{-1}$, in the spectrum of Fig. 3. Their peak at $48{,}645\ \mathrm{cm}^{-1}$ appears in Fig. 3 to be an un-

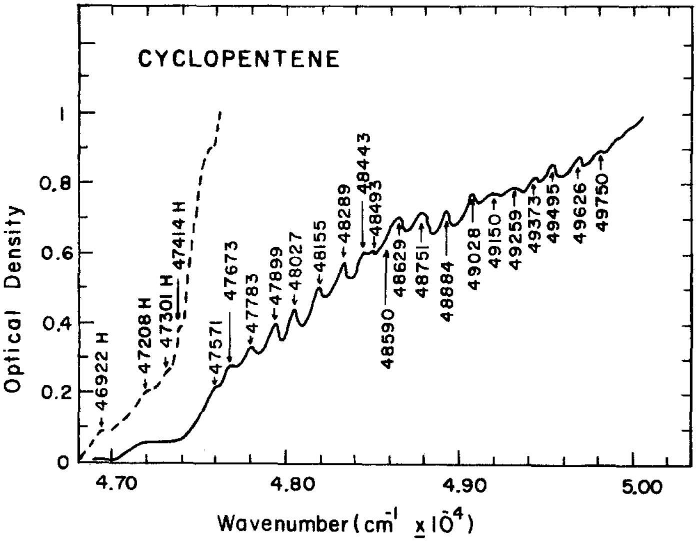


Fig. 3. The $R(3s) \leftarrow N$ transition of cyclopentene vapor at 20° C. Band positions are quoted in cm^{-1}

resolved doublet with maxima estimated at 48,590 and 48,629 cm^{-1}. In addition, four new peaks are reported at 46,922, 47,208, 47,301 and 47,414 cm^{-1}. By cooling the vapor to about 0° C, it was determined that these four peaks, plus the 48,443 cm^{-1} member of the resolved doublet, are hot bands. Lowering the temperature failed to resolve the second apparent doublet. The band estimated to be at 48,629 cm^{-1} may or may not be hot. Heating the vapor to 140° C resulted in a smearing-out of vibrational structure and revealed no other hot bands.

As shown in column 3 of Table 4, two very regular progressions have been found and assigned as quanta of the ring-puckering vibration ν_p. The first progression is built on the band at 47,571 cm^{-1} which, being the first non-hot band, is taken to be the $(0, 0')$ transition. The other progression is built on the band at 49,028 cm^{-1}. This band is 1457 cm^{-1} above the $(0, 0')$ position and represents a new frequency which needs assignment (see column 4, Table 4). A third progression is also observed in the ν_p frequency. It appears to be built on a band located at about 48,289 cm^{-1}. This band, see column 4, is 718 cm^{-1} above the $0, 0'$ energy.

The hot bands have been tentatively assigned as shown in column 1 of Table 4. The band at 47,417 cm^{-1}, being 157 cm^{-1} to the red of the $(0, 0')$, is assigned as $3\nu_p$ in the ground state. Laane and Lord [7] report this ground state frequency to be 152.6 cm^{-1}. The band at 47,301 cm^{-1} is diffuse (maximum 270 cm^{-1} from the $(0, 0')$) and might result from an overlapping of $4\nu_p$ and $5\nu_p$ bands which are reported by Laane and Lord [7] to be at 235 and 312 cm^{-1}, respectively. The band at 47,208 cm^{-1} is 363 cm^{-1} to the red of the $(0, 0')$ and is assigned as ν_T which is reported by Beckett, Freeman and Pitzer [6] to have a ground state frequency of 386 cm^{-1}. The initial hot band at 46,922 cm^{-1} corresponds to ground state frequency of 549 cm^{-1}. This might correspond to a ring-bending mode reported [13] at 607 cm^{-1}.

The "hot" member of the resolved doublet (48,443 cm^{-1}) is 147 cm^{-1} to the red of the band at 48,590 cm^{-1}; this frequency is again assigned as $3\nu_p$ in the ground state. The band at 48,590 cm^{-1} is 1019 cm^{-1} above the $(0, 0')$ as shown in column 4.

If the shoulder of the unresolved doublet at 48,629 cm^{-1} is hot, then it appears to be one ground state quantum of ν_T built on the band at 49,028 cm^{-1} (1457 cm^{-1} above the $(0, 0')$).

If the band at 48,629 cm^{-1} is not hot, it may be incorporated, as previously specified, into another apparent progression in ν_p as shown in column 3. This necessitates the assumption that the band at 48,289 cm^{-1} (on which the progression is built) is a new frequency of 718 cm^{-1}.

As seen in column 4, we now have two or three unassigned frequencies: 718, 1019, and 1457 cm^{-1}. The C=C stretching frequency in the ground state has been reported by Beckett, Freeman and Pitzer [6] to be 1623 cm^{-1}. We are unable to predict how much this will be decreased in the excited state. If it is greatly reduced, then the frequencies of 718 and 1457 cm^{-1} might represent single and double excitations of this mode. If it is not so greatly reduced, then either the 1019 or 1457 cm^{-1} frequency may correspond to one quantum of C=C stretch. We assume that the 1457 cm^{-1} frequency is the best candidate for such an assignment.

Laane and Lord [7] have reported that the $n = 0$ and 1 levels of the puckering vibration in the ground state are nearly degenerate (0.91 cm^{-1} separation). In

Table 4. *Vibrational analysis of the R(3s)←N transition in cyclopentene*[a]

Hot frequencies	Observed bands (cm^{-1})	Progressions						Tentative assignment[b]	Other frequencies
549, (1, 0') ring bending	46922 H								
363, (1, 0') ν_T	47208 H								
270, (4, 0') and (5, 0') ν_p	47301 H								
157, (3, 0') ν_p	47414 H								—
—	47571 (0, 0')	—							
	47673	102	—					(0, 1') ν_p	
	47783	212	110	—				(0, 2') ν_p	
	47899	328		116	—			(0, 3') ν_p	
	48027	456			128	—		(0, 4') ν_p	
	48155	584				128	—	(0, 5') ν_p	
	48289	718	—				134	(0, 6') ν_p	718
147, (3, 0') ν_p	48443 H								
	48493		204	—				(0, 2') ν_p	
—	48590		301	97				(0, 3') ν_p	1019 (?)
399, (1, 0') ν_T (?)	48629 H (?)		340	136	—				
	48751		462			122	—	(0, 4') ν_p	
	48884		595				132	(0, 5') ν_p	
—	49028	—							1457
	49150	122	—					(0, 1') ν_p	
	49259	231	109	—				(0, 2') ν_p	
	49373	345		116	—			(0, 3') ν_p	
	49495	467			122	—		(0, 4') ν_p	
	49626	598				131	—	(0, 5') ν_p	
	49750	722					124	(0, 6') ν_p	

[a] Horizontal lines indicate the band on which a progression is built or from which a frequency difference is computed; H indicates hot bands; primed numbers indicate excited state vibrational quanta, unprimed numbers indicate ground state vibrational quanta.

[b] These assignments are made here merely to indicate regularity. The alternative assignments made in the text are as follows:

(i) If a double-minimum exists in both the *N* and *R* states for the $Q(\nu_p)$ normal coordinate, and if corresponding near-degeneracies of ν_p vibrational levels also occur in the *R* state, then these series members, in order of increasing energy, can be labelled 0→0', 0→2', 0→4', etc. *or* 1→1', 1→3', 1→5', etc. Both of these progressions are totally symmetric and should be interspersed to yield an apparently regular progression with an (unresolvable) interval of ~1 cm^{-1} between the corresponding members of the odd and even series. Vibronic allowedness of the electronic transition is not required in this point of view.

(ii) As in (i), but with series labelling 1→0', 1→2', 1→4', etc. *or* 0→1', 0→3', 0→5', etc. Each member of either progression is now non-totally symmetric. Case (ii) cannot be distinguished from case (i) using the present data. Vibronic allowedness of the electronic transition is required in the point of view of case (ii).

(iii) A possibility not discussed in the text emphasizes the regular nature of the progressions and their slight but obvious positive anharmonicity. One might assume that no double minimum exists in the excited state and that, in fact, the $Q(\nu'_p)$ coordinate exhibits only one rather flat-bottomed potential minimum. In this instance, one would expect a rather lengthy progression in ν'_p and one should label the series as 0→0', 0→1', 0→2', 0→3', etc. *or* 1→0', 1→1', 1→2', 1→3', etc. where the puckering vibration is now considered to be a totally symmetric vibration of puckered cyclopentene. In this instance also, no vibronic-allowedness considerations are required.

addition, the $n = 2$ and 3 levels are separated by only 25.2 cm^{-1}. From the spacing observed in the regular progressions, we must assume that the puckering potential barrier is much less in the excited state.

Discussion of Vibronic Stealing in Relation to the Rydberg Spectra of Mono-Olefins

We have seen that one of the two assignments (ν_p or ν_T), or a combination of them, must be used to explain the structure on the $R(3s) \leftarrow N$ transition in cyclopentene. In our coordinate frame [1] the symmetry operators in C_{2v} become E, $C_2(y)$, $\sigma_v(xy)$ and $\sigma_v'(yz)$. Under these operations the $R(3s) \leftarrow N$ transition is $A_1 \rightarrow B_1$ and is x-allowed; the $V \leftarrow N$ transition is $A_1 \rightarrow B_2$ and is z-allowed; ν_p is of b_1 symmetry; and ν_T is of a_2 symmetry. We must now explain why a nominally non-totally symmetric vibration should dominate the observed structure in a formally-allowed transition.

Clearly, the torsional mode or the puckering vibration (or a combination of the two) resembles the molecular distortion which occurs on electronic excitation to the Rydberg state and, thus, strongly couples to the electronic transition. The ring-puckering mode is known to exhibit near-degeneracy of the 0 and 1 vibrational levels in the ground electronic state [7]. Therefore, assuming that it is indeed the puckering mode which is excited, totally symmetric vibrational transitions of the form $0 \rightarrow 2'$, $1 \rightarrow 3'$, $0 \rightarrow 4'$, $1 \rightarrow 5'$, etc., could accompany the allowed electronic transition, and could appear as a progression in nominally-single vibrational quanta because of the near degeneracy of the 0 and 1 vibrational levels in the ground state. And yet, we cannot see why other totally symmetric vibrations, such as $C=C$ stretching, should not be just as prevalent in the vibrational structure. In this regard, we emphasize that the only evidence for vibrations other than ν_p is indirect and is associated with the necessity of having initiation points for the two higher-energy progressions in ν_p.

An alternative explanation is provided by the vibronic stealing mechanism. A non-totally symmetric vibration would dominate the observed structure if most of the intensity was obtained *via* the vibronic-stealing mechanism. The ν_T vibration can couple to the $R(3s) \leftarrow N$ transition, making it vibronically z-allowed and enabling it to steal intensity from the $V \leftarrow N(\pi \rightarrow \pi^*)$ located at 5.34 eV. The ν_p vibration can couple to the $R(3s) \leftarrow N$ transition, making it vibronically y-allowed and enabling it to steal intensity from the $\pi \rightarrow \pi''$ transition assigned [1] at 7.36 eV. No matter which vibrational assignment is accepted (ν_p or ν_T, or both), this mechanism explains the predominance of non-totally symmetric vibrations. In this instance, however, the members of the progression must be assigned as $1 \rightarrow 2'$, $0 \rightarrow 3'$, $1 \rightarrow 4'$, $0 \rightarrow 5'$, ... etc. in $\nu_p \rightarrow \nu_p'$ and *not* as given in Table 4.

In this latter vein, cyclopentene is assumed not to be atypical but to behave much like other olefins. The apparent difference from other olefins is then attributed to the happenstance that cyclopentene is the only molecule studied in which the totally symmetric vibrations differ greatly in energy from the non-totally symmetric ones which might mediate vibronic stealing.

We have not analyzed the vibrational structure on the Rydberg bands in the methyl-substituted olefins. It is known [9] that the isomeric butenes possess vibrational modes of the correct symmetry to allow stealing from the $V \leftarrow N$

transition; furthermore, these modes are energetically of the same order of magnitude as the totally symmetric C=C stretching mode and the meagre vibrational data which exists (see Fig. 2) does not allow any meaningful distinction to be made between the coupling of symmetric or antisymmetric vibrations. However, we should emphasize that the intensity calculations [1] (using $\zeta_{3s}=0.483$) do agree well with experiment for the isomeric butenes; consequently, if vibronic stealing is present in these systems, it and the direct electronic dipole allowedness should be of comparable importance.

The topic of vibronic stealing in ethylene itself is also a relevant question [1]. Prior calculations [1] indicate that the intensity of the $V \leftarrow N$ band can only be accounted for using a vibronic mechanism. However, Merer [3, 10] has provided an interpretation of the vibrational structure associated with this band and this interpretation does not depend on any vibronic intensity-stealing mechanism whatever. While we can provide interpretations which do invoke vibronic coupling, we cannot do better than the Merer-Mulliken assignment. Hence, at least for the present, we desist in this effort.

In summary, calculations discussed [1] in paper I indicate that the intensity of the $R \leftarrow N$ band of ethylene and many of its methyl derivaitves may be vibronically induced. Vibrational structure in the methyl-substituted ethylenes is inadequate to discriminate the nature of the intensity in the $R \leftarrow N$ bands of these compounds. The vibrational structure in cyclopentene can be construed as indicative of vibronic induction of intensity in the $R \leftarrow N$ system of this molecule; unfortunately, as we have shown, this conclusion is certainly not unambiguous. The vibrational structure in the $R \leftarrow N$ band of ethylene can be interpreted [10] without recourse to a vibronic coupling mechanism; indeed, if the $R \leftarrow N$ bands of C_2H_4 are [3] unambiguously of type C, it is unlikely that any vibronic coupling mechanism is operative in this molecule. An evaluation of these various data indicates to us the necessity for further investigative effort.

Summary of Results

Our results may be summarized as follows:

(i) Experimental intensities and excitation energies of the initial, weak absorption in liquid olefins are more consistent with an $R^* \leftarrow N$ ($\pi \rightarrow \sigma^*$) assignment than with either an $T \leftarrow N$ or $T_R \leftarrow N$ assignments.

(ii) Some $T \leftarrow N$ and $T_R \leftarrow N$ absorption bands may have been located (see Fig. 1 and Table 2).

(iii) Experimentally determined f-numbers for the $R(3s) \leftarrow N$ transition in mono-olefins do not agree with those calculated [1] on the basis of dipole-allowedness. These intensities can be explained [1] by assuming that the $R(3s) \leftarrow N$ transition gains some intensity *via* vibronic stealing from the $V \leftarrow N$ transition. This vibronic stealing mechanism also offers explanation of the vibrational structure observed in the Rydberg spectrum ($R \leftarrow N$) of cyclopentene.

(iv) Both computations and self-pressure studies indicate that the Rydberg 3*s* orbital may not be as diffuse or as atomic-like as is usually assumed. The *R* state apparently possesses considerable valence-shell character.

(v) A moderately well-resolved spectrum of the $R(3s) \leftarrow N$ transition in cyclopentene reveals the presence of several hot bands and at least two regular progressions which we assign to the ring-puckering vibration, ν'_p, of the excited R state.

References

1. Watson, Jr., F. H., Armstrong, A. T., McGlynn, S. P.: Theoret. chim. Acta (Berl.) **16**, 75 (1970).
2. Ross, K. J., Lassetre, E. N.: J. chem. Physics **44**, 4633 (1966).
3. Merer, A. J., Mulliken, R. S.: Chem. Reviews **69**, 639 (1969).
4. Itoh, M., Mulliken, R. S.: In press, private communication.
5. Evans, D. F.: J. chem. Soc. (London) **1960**, 1735.
6. Beckett, C. W., Freeman, N. K., Pitzer, K. S.: J. Amer. chem. Soc. **70**, 4227 (1948).
7. Laane, J., Lord, R. C.: J. chem. Physics **47**, 4941 (1967).
8. Carr, E. P., Stücklen, H.: J. chem. Physics **6**, 55 (1938).
9. Kilpatrick, J. E., Pitzer, K. S.: J. National Bureau of Standards **38**, 191 (1947).
10. Merer, A. J., Schoonveld, L.: J. chem. Physics **48**, 522 (1968).

Professor S. P. McGlynn
Coates Chemical Laboratories
Louisiana State University
Baton Rouge, Louisiana 70803, U.S.A.