Raman Spectra of Acetylenic Bromides, Iodides, and Ketones and of Some Cyclic Compounds

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where

$$\beta_{nm}=\sum_{k=1}^{p} e_k P_n^m(\lambda_k) P_n^m(\mu_k) \cos m\varphi_k, \quad (33)$$

$$\beta'_{nm}=\sum_{k=1}^{p} e_k P_n^m(\lambda_k) P_n^m(\mu_k) \sin m\varphi_k. \quad (34)$$

Then, from Eqs. (29) to (32),

$$B_{nm}=\frac{2D_{nm}\beta_{nm}}{R}\left(\frac{1}{D}-\frac{1}{D_i}\right)\left[\frac{P_n^m(\lambda_0)}{Q_n^m(\lambda_0)}-\left(\frac{D_i}{D}\right)\frac{P_n^{m\prime}(\lambda_0)}{Q_n^{m\prime}(\lambda_0)}\right]^{-1}=f(\beta_{nm}), \quad (35)$$

$$B'_{nm}=f(\beta'_{nm}). \quad (36)$$

The electrostatic free energy of the molecule is

$$W=\frac{1}{2}\sum_{k=1}^{p} e_k\psi_i(\lambda_k, \mu_k, \varphi_k), \quad (37)$$

where $\psi_i(\lambda_k, \mu_k, \varphi_k)$ is the value of ψ_i at $(\lambda_k, \mu_k, \varphi_k)$ due to all charges except e_k. W can be written as the sum of the separate contributions of each possible interaction, as in Eqs. (1) and (2). Then, corresponding to Eq. (3), for the interaction between the jth and kth charges

$$\frac{1}{D_E(jk)}=\frac{1}{D_i}+2\left(\frac{r_{jk}}{R}\right)\left(\frac{1}{D}-\frac{1}{D_i}\right)\times\sum_{n=0}^{\infty}\sum_{m=0}^{n} P_n^m(\mu_j)P_n^m(\lambda_j)P_n^m(\mu_k)P_n^m(\lambda_k)\times T_{nm}(\lambda_0)\cos m(\varphi_j-\varphi_k) \quad (38)$$

in which

$$T_{nm}(\lambda_0)=D_{nm}\left[\frac{P_n^m(\lambda_0)}{Q_n^m(\lambda_0)}-\left(\frac{D_i}{D}\right)\frac{P_n^{m\prime}(\lambda_0)}{Q_n^{m\prime}(\lambda_0)}\right]^{-1} \quad (39)$$

and r_{jk} is the distance between e_j and e_k. Recurrence formulas are found to be of considerable aid in applying Eq. (38).

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Raman spectra are listed for series of acetylenic bromides, iodides, and ketones, and for ascaridole, 1,3-dioxane, ethyl-*p*-toluenesulfonate, and for the *cis*- and *trans*-1,2-diacetoxycyclohexanes. Depolarization factors (when obtained) and relative intensities were measured by use of a Gaertner microdensitometer.

DURING the course of several investigations carried on in this laboratory, there have been obtained the Raman spectra of a miscellany of compounds, data for which do not appear in the literature. Part of the work reported here represents preliminary investigations on series of compounds whose spectra did not exhibit the particular anticipated qualities. Other spectra were obtained on intermediates employed in the synthesis of diverse compounds.

The method of obtaining the spectra has been described elsewhere.[1] The results are listed in Tables I–III, in which $\Delta\nu$ is given in cm^{-1}; ρ is the depolarization factor and I is the intensity measured by use of a Gaertner microdensitometer; D and P represent lines that were depolarized or polarized, respectively, but for which no accurate measurement could be made; w is the designation for lines too weak for densitometer readings; and b means an unusually broad line. In each case the strongest line on the plate is arbitrarily given an intensity of 100.

ACETYLENIC BROMIDES[2]

R—C≡C—Br

These halides, whose spectra are listed in Table I, were prepared by the general method of Straus, Kollek, and Heyn.[3] It was found unnecessary, however, to use soap for emulsifying the hydrocarbon provided the reaction mixture was stirred vigorously.

[1] F. F. Cleveland, M. J. Murray, J. R. Coley, and V. I. Komarewsky, J. Chem. Phys. **10**, 18 (1942).

[2] For the spectrum of the first member of this series see F. F. Cleveland and M. J. Murray, J. Chem. Phys. **11**, 450 (1943).

[3] F. Straus, L. Kollek, and W. Heyn, Ber. **B63**, 1868 (1930).

TABLE I. Raman spectra of acetylenic bromides and iodides.

$C_2H_5C\equiv CBr$		$C_2H_5C\equiv CI$			$C_3H_7C\equiv CBr$		$C_3H_7C\equiv CI$		$C_4H_9C\equiv CBr$			$C_4H_9C\equiv CI$		$C_5H_{11}C\equiv CBr$		$C_5H_{11}C\equiv CI$			$C_6H_5C\equiv CBr$	
$\Delta\nu$	I	$\Delta\nu$	I	ρ	$\Delta\nu$	I	$\Delta\nu$	I	$\Delta\nu$	I	ρ	$\Delta\nu$	I	$\Delta\nu$	I	$\Delta\nu$	I	ρ	$\Delta\nu$	I
263	13	242	10	0.7	255	3	227	w	249	3	P	230	3	241	w	218	2		267	w
351	16	349	20	0.8	347	30	341	28	341	18	0.75	346	20	346	35	346	13	0.6	356	w
		380	8	0.4			378	6	370	2	P					380	w			
417	7	417	w		417	6	406	6	417	1		417	1							
									452	1		450	w							
545	1	530	3	0.9			543	2	567	1	P	559	1	564	1	554	2	D		
																			622	w
704	w	701	w																	
780	2	782	2	0.8					807	2	0.31	811	3							
					846	2	846	4	852	w				835	2	832	2	P	837	w
					878	2	877	6	871	1	P	876	1							
908	8	892	2	0.7					895	1	P	896	1							
									926	1		923	1							
							964	w	947	1		955	1			964	w			
							1002	w								987	w		999	10
1046	16	1037	6	0.5	1062	w	1056	2	1064	3	0.4	1060	3	1047	w	1041	1			
1080	5	1074	3	0.6										1073	w	1071	2			
					1091	3	1094	5	1100	5	0.55	1104	5	1112	2	1108	2	0.7	1178	3
							1227	w	1238	1		1239	w						1229	12
1260	w	1256	1	0.9			1262	2				1280	w							
									1291	2	D	1299	1	1302	5	1301	2			
1318	14	1314	6	0.8	1325	w	1327	6	1324	5	0.55	1324	7	1328	5	1326	3	0.7		
1382	3	1380	1	0.8			1355	w												
1436	11	1433	5	0.7	1428	4	1427	8	1430	8	0.9	1427	7	1435	15	1435	6	0.7		
1461	11	1458	3	0.7	1453	4	1451	7	1446	7		1448	6	1458	10	1455	4		1597	32
2114	w	2101	w																	
		2186	100	0.3			2192	100				2190	100			2191	100	0.3		
2210	100	2212	18	0.4	2217	100			2215	100	0.38			2219	100				2201	100
2224																				
2734	w	2732	w	P					2732	w										
2842	9	2840	3	0.2	2828	w	2832	5	2830	3	P	2826	3	2854	20	2861	20b	0.25		
2881	17	2882	12	0.3	2873	25	2869	17	2863	22	0.3	2863	20	2867	40					
2920	60	2912	35	0.3	2909	40	2903	50	2904	50	0.47	2905	50	2905	70	2904	50	0.3		
2938	50	2937	25	0.3	2935	40	2933	40	2928	45	0.33	2929	20	2928	60	2926	30	0.3		
2986	22	2982	15	0.9	2966	10	2966	9	2961	12	0.62	2964	5	2967	15	2961	10	0.6	3062	15

1-Bromo-1-butyne,

C_2H_5—C≡C—Br, b.p. 90–91° at 750 mm.

1-Bromo-1-pentyne,

C_3H_7—C≡C—Br, b.p. 117° at 750 mm.

1-Bromo-1-hexyne,

C_4H_9—C≡C—Br, b.p. 74° at 72 mm.

1-Bromo-1-heptyne,

C_5H_{11}—C≡C—Br, b.p. 71–73° at 22 mm.

1-Bromo-2-phenylethyne,

C_6H_5—C≡C—Br, b.p. 68–69° at 3 mm.

ACETYLENIC IODIDES[2]

R—C≡C—I

These halides, whose spectra are also listed in Table I, were prepared from the acetylenic Grignard reagent by the action of iodine in ether solution. The method is that of Grignard and Perrichon.[4]

1-Iodo-1-butyne,

C_2H_5—C≡C—I, b.p. 65.5–66.0° at 75 mm.

1-Iodo-1-pentyne,

C_3H_7—C≡C—I, b.p. 75–76° at 45 mm.

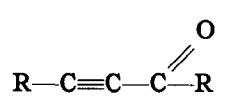
1-Iodo-1-hexyne,

C_4H_9—C≡C—I, b.p. 74° at 16 mm.

1-Iodo-1-heptyne,

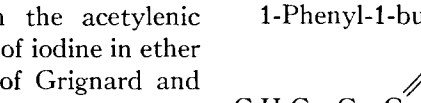
C_5H_{11}—C≡C—I, b.p. 91° at 18 mm.

ACETYLENIC KETONES[5]



These ketones were prepared and their spectra obtained by R. E. Dineen. The synthetic method used was that of Kroeger and Nieuwland,[6] in which an anhydride is reacted with the aryl- or alkylacetylenemagnesium chloride.

1-Phenyl-1-butyn-3-one,



$C_6H_5C\equiv C-C(=O)-CH_3$, b.p. 79.0–79.4° at 2 mm, n_D^{24} 1.5730.

[4] V. Grignard and H. Perrichon, Ann. Chim. Phys. **5**, 5 (1926).

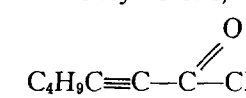
[5] For the spectrum of 6-dodecyn-5-one, see M. J. Murray and F. F. Cleveland, J. Am. Chem. Soc. **63**, 1363 (1941).

[6] J. W. Kroeger and J. A. Nieuwland, J. Am. Chem. Soc. **58**, 1861 (1936).

TABLE II. Raman spectra of acetylenic ketones.

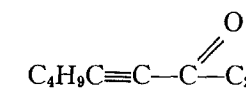
1-Phenylbutyn-3-one Δν	I	ρ	3-Hexyn-2-one Δν	I	3-Octyn-2-one Δν	I	ρ	4-Nonyn-3-one Δν	I	ρ
167	1.0		193	6b	207	1b				
208	0.7		226	8b	261	w				
296	0.2				319	3				
364	2		357	3b	354	7b		349	2b	0.8
395	0.3				378	4		371	2	
435	1.0		406	1b	423	1		428	½b	
469	0.3				441	2				
514	0.7		511	1						
533	1.7									
583	1.5		585	3	587	4				
590	1.2									
622	1.7		659	3	658	1		626	w	
678	1.1									
759	1.4		782	½	809	3b		804	2	0.3
					872	1		870	w	
852	1.4		906	½	898	1		892	w	
					924	1		926	2	P
978	18	0.22	974	20	948	4		958	½	
					974	10b				
997	15	0.15								
1026	0.9		1037	3				1013	1	
								1047	2b	0.6
1063	0.2		1068	3	1059	4		1071	1	
1156	25	0.3			1106	7		1105	2	0.8
								1173	w	
1178	2				1234	3		1235	½	
1264	6b	0.35			1299	1		1295	1	D
			1314	3	1325	6		1323	2	D
			1376	2	1356	1				
1442	0.7		1430	8	1424	8	D	1421	4b	D
1492	6	0.5	1460	6	1446	7	D	1451	5b	D
1593	60	0.4								
1684	33	0.3	1676	75	1675	100	0.4	1674	30	0.4
2125	7	0.4								
2169	w				2170	w				
2205	100	0.4	2211	100	2212	100	0.4	2212	100	0.4
			2227	30						
2257	w		2269	2	2262	4		2247	5	
2342	w									
2448	w									
2498	w									
2561	0.7									
					2824	w				
			2885	10	2863	20	P	2865	30	
2917	5	0.2	2919	75	2910	100b	0.4	2903	60	
			2941	30	2934	40		2937	70	
2965	w				2964	15	D	2977	13	
3000	w		2990	10b	3007	4				
3064	8	0.45								
3184	0.4									

3-Octyn-2-one,



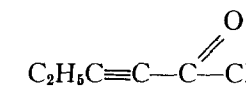
$C_4H_9C{\equiv}C{-}C{-}CH_3$, b.p. 75–77° at 14–16 mm, n_D^{23} 1.4459.

4-Nonyn-3-one,



$C_4H_9C{\equiv}C{-}C{-}C_2H_5$, b.p. 92–94° at 15 mm, n_D^{23} 1.4484.

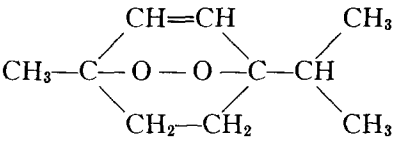
3-Hexyn-2-one,



$C_2H_5C{\equiv}C{-}C{-}CH_3$, b.p.[7] 77.0–78.5° at 73 mm, n_D^{25} 1.4371.

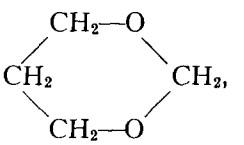
[7] The boiling point of 76° at 15 mm and n_D^{25} 1.4460 as given for this compound by J. W. Kroeger, F. S. Sowa, and J. A. Nieuwland, J. Org. Chem. **1**, 163 (1936) appear to be in error since these are almost exactly the same boiling point and index of refraction given by Kroeger and Nieuwland (reference 6) and by the present investigators for 3-octyn-2-one.

ASCARIDOLE



The sample investigated was an Eastman Kodak Company product. It was distilled in vacuum directly into the Raman tube with no attempt at fractionation.

1,3-DIOXANE



1,3-Dioxane (trimethyleneformal).

The sample used was an Eastman Kodak Company product which was carefully fractionated, b.p. 104.7–105.0° at atmospheric pressure. The spectrum, listed in Table III, was obtained by R. H. Saunders.

TABLE III. Raman spectra of some cyclic compounds.

1,2-Diacetoxycyclohexane *cis* Δν	I	*trans* Δν	I	1,3-Dioxane Δν	I	ρ	Ascaridole Δν	I	Ethyl *p*-toluenesulfonate Δν	I	ρ
234	2b	217	1						229	20	0.3
285	w	248	w								
318	3	276	1	273	2	D	315	w	336	w	
361	1	365	4						373	7	0.7
381	1										
430	1	441	1	439	2	P	438	2			
467	1			461	4	D	463	4	477	w	0.8
503	1	531	4	491	7	0.6	547	1			
568	3	559	1				583	1			
605	2	604	1						633	20	0.9
626	2	638	2	649	w	D			657	3	
666	1	661					728	30	751	w	
792	2	798	2						791	30	0.15
821	4	815	w				816	4	810	14	0.3
849	1	842	2	834	100	0.2	878	6			
884	3	892	4	905	8	0.7	893	4			
921	2b	914	3				938	w			
954	1	957	1	988	35	0.25					
986	2	991	1								
1015	w			1011	10	D					
1029	5	1040	4	1046	6	D					
1055	w	1060	3				1064	1			
1072	2	1100	w	1092	10	D			1099	25	0.25
1122	1						1128	7			
1147	1	1148	4	1154	7	D			1173	100	0.2
1172	w								1188	25	
1207	1	1216	2	1207	4	D	1207	5	1210	3	
1257	4	1249	3	1230	7	D					
		1271	w	1296	20	D					
		1300	w	1312	15				1349	w	
1310	2	1318	w				1312	w	1380	7	P
1343	2b	1354	2	1408	w	D	1344	w			
1386	2	1388	2	1433	10	D	1380	w	1445	4	
1448	4	1449	6	1463	30	D	1450	12	1462	4	
1735	3	1734	4	2747	4		1623	12	1598	60	0.75
2856	12	2865	18	2783	10	0.15	2874	40	2764	w	P
2910	10	2905	10	2852	80b	0.25	2934	100	2928	30	0.15
				2926	50	0.35			2982	6	0.7
2943	100b	2945	100b	2958	30		2961	65	3038	3	
				2985	75b	0.4	3051	17	3070	18	0.5

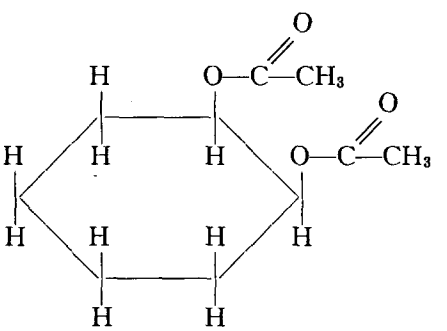
ETHYL *p*-TOLUENESULFONATE

Ethyl *p*-toluenesulfonate,

$$CH_3—C_6H_4—SO_2OC_2H_5.$$

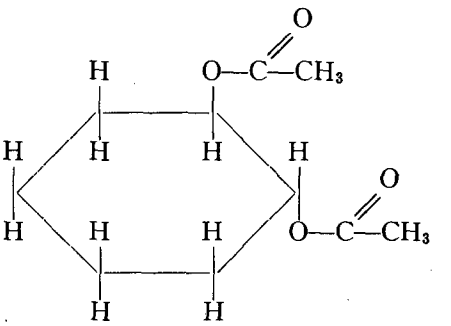
Prepared by Charles Jones by the action of an ether solution of *p*-toluenesulfonylchloride on ethyl alcohol in the presence of sodium hydroxide. B.p. 143° at 2–3 mm. The spectrum is given in Table III.

cis- AND *trans*-1,2-DIACETOXYCYCLOHEXANE



cis-1,2-Diacetoxycyclohexane.

Synthesized by acetylation of the corresponding *cis*-glycol by Howard Hess, who also obtained the spectrum of the compound. B.p. 117.8–118.0° at 12 mm, n_D^{25} 1.4475.



trans-1,2-Diacetoxycyclohexane.

Synthesized by the action of silver acetate on the *trans*-bromohydrin by Robert Buckles, who also obtained the spectrum of this compound. B.p. 119.8–120.0° at 12 mm, n_D^{25} 1.4458.

ACKNOWLEDGMENT

The authors wish to acknowledge the work of the several students who prepared and obtained the spectra of a number of the compounds.

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Accommodation Coefficients on Gas Covered Platinum *

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(Received March 1, 1944)

Accommodation coefficients on a platinum wire have been computed for five monatomic and five diatomic gases from Pirani gauge measurements at room temperature, 18.9° to 30.5°C. Through careful control of experimental conditions it was possible to apply exact theoretical relations for the effects of radiation, wire conduction, and free molecule conduction upon the temperature distribution along the gauge wire. For each of the gases the accommodation coefficient increases with pressure up to about 0.1 mm and then remains constant throughout the pressure range in which complete free molecule conduction exists, indicating the absence of complete gas saturation of the wire surface at the lower pressures. There is no detectable temperature coefficient in the small interval in which measurements were made. At room temperature the mean accommodation coefficients on a completely gas covered platinum wire are: helium, 0.403±0.001; neon, 0.700±0.002; argon, 0.847±0.002; krypton, 0.844±0.002; xenon, 0.858±0.002; hydrogen, 0.312±0.001; deuterium, 0.393±0.001; nitrogen, 0.769±0.002; carbon monoxide, 0.772±0.002; oxygen, 0.782±0.002.

ACCURATE values of accommodation coefficients of gases on solids are required for the estimation of energy transport by gases at low pressures. Values for gas covered platinum wire are of particular interest since a heated platinum wire is used frequently as an energy

* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 506.