The corresponding methiodide was prepared by adding 2 g. of methyl iodide to 1 g. of the amine ether, and allowing the mixture to stand for forty-eight hours. The benzyl chloride and the benzyl bromide were obtained by heating 1 g. of the amine ether with 2 g. of the benzyl halide for eight hours. The salts were recrystallized from ethyl acetate.

TABLE I

4-[β-OXY-ETHYL]-MORPHOLINE

Compound	Formula	M. p., °C. (uncor.)	Analyses, % N Calcd.	Analyses, % N Found
	O-Dodecyl-			
Hydrochloride	$C_{18}H_{38}O_2NCl$	97	4.17	3.99
Hydrobromide	$C_{18}H_{38}O_2NBr$	105	3.69	3.53
Oxalate	$C_{20}H_{39}O_6N$	108	3.29	3.39
Picrate	$C_{24}H_{40}O_9N_4$	62	10.60	10.53
Methiodide	$C_{19}H_{40}O_2NI$	56	3.17	3.10
Benzyl chloride	$C_{25}H_{44}O_2NCl$	96	3.29	3.51
Benzyl bromide	$C_{25}H_{44}O_2NBr$	105	2.98	2.98
	O-Tetradecyl-			
Hydrochloride	$C_{20}H_{42}O_2NCl$	112	3.85	3.85
Hydrobromide	$C_{20}H_{42}O_2NBr$	115	3.43	3.55
Oxalate	$C_{22}H_{43}O_6N$	109	3.35	3.52
Picrate	$C_{26}H_{44}O_9N_4$	80	10.07	9.96
Methiodide	$C_{21}H_{44}O_2NI$	73	2.98	3.20
	O-Hexadecyl-			
Hydrochloride	$C_{22}H_{46}O_2NCl$	105	3.59	3.37
Hydrobromide	$C_{22}H_{46}O_2NBr$	112	3.22	3.17
Oxalate	$C_{24}H_{47}O_6N$	112	3.16	3.21
Picrate	$C_{28}H_{48}O_9N_4$	78	9.62	9.48
Methiodide	$C_{23}H_{48}O_2NI$	80	2.83	2.83

DEPARTMENT OF CHEMISTRY
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The Aqueous Solubility of Hydrated Chromic Nitrate at 25°

BY NORMAN O. SMITH

In connection with the recrystallization of chromic nitrate the author was surprised to discover that there is no information in the literature as to the solubility of this common salt. The following solubility determination was therefore carried out.

Samples of J. T. Baker Analyzed chromic nitrate nonahydrate were rocked in a 15-ml. glass-stoppered tube in a thermostat at 25 ± 0.03° for several days. Equilibrium was approached from both under- and over-saturation and concentrations were measured by means of chromium analyses. Chromium was determined by oxidation to chromate with sodium peroxide followed by the iodometric determination of the chromate. The resulting values of the solubility were

	Wt., % $Cr(NO_3)_3$
From undersaturation	44.95
From oversaturation	44.71
	Av. 44.83

The solid phase was removed by filtration, centrifuged, air-dried for ten minutes and then analyzed. It was found to contain 59.33% $Cr(NO_3)_3$. Calculated for $Cr(NO_3)_3 \cdot 9H_2O$: 59.48% $Cr(NO_3)_3$. The solid phase is therefore the nonahydrate.

Apparently hydrolysis is not sufficient to produce any solid basic compound. Furthermore, the ready attainment of equilibrium distinguishes the behavior of the nitrate from that of several other chromic compounds.[1,2,3]

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(1) Olie, *Z. anorg. Chem.*, **51**, 29 (1906).

(2) Montemartini and Vernazza, *L'Industria chimica*, **8**, 445 (1933).

(3) Hill, Smith and Ricci, THIS JOURNAL, **62**, 858 (1940).

DEPARTMENT OF CHEMISTRY,
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On Phosphorescence Vibration Spectra of Polyatomic Molecules

BY O. REDLICH AND E. K. HOLT

A few more details can be read from the phosphorescence vibration spectra recently published and interpreted by Lewis and Kasha[1] on the basis of the principle of Franck and Condon.

(1) For a complete interpretation, the analysis of the vibration spectra and the knowledge of the parameters of the phosphorescent state is required. If x denotes a $(3n - 6)$-dimensional vector representing the elongations in internal geometric coördinates, and $q = Ax$ is the vector of the normal coördinates, then the vector $p = Bx$ representing the distortion of the phosphorescent molecule determines, according to the Franck–Condon principle, the amplitudes $q_v = AB^{-1}p$ of the vibrations excited in the transition to the ground state. The quantum number v of the k^{th} vibration is given by $2v + 1 = 3(q_v^k/q_1^k)^2$ where q_1^k denotes the amplitude of the first quantum state. This somewhat crude application of the Franck–Condon principle should furnish a fair approximation if, as in the measurements of Lewis and Kasha, only the zero-point vibration of the phosphorescent molecule is excited.

The distortion p can be represented as a vector in the space spanned by the amplitudes q_1^k. If p has a lower symmetry than q_1, the vector p lies in the subspace spanned by those amplitudes which are symmetric with respect to the phosphorescent molecule. Only the corresponding vibrations are excited. Provided the symmetry of p is not higher than that of q_1, the totally symmetric vibrations are always permitted. If p has no symmetry element, all vibrations are permitted. The interpretation of the phosphorescent molecule as a biradical suggests the assumption that a center of symmetry, if present in the ground state, is maintained in the phosphorescent state.

(2) For a crude analysis of the spectrum of benzene, approximate normal coördinates are derived from the assumptions that the vibrations are carried out either by the rigid CH groups or by the hydrogens against the carbons, and that they are either stretching or bending vibrations. The

(1) G. N. Lewis and M. Kasha, THIS JOURNAL, **66**, 2100 (1944).

simplest models of the phosphorescent state are planar and based on the assumption that the aromatic bonds (1.40 Å.) are changed to two double bonds (1.33 Å.) and four single bonds (1.54 Å.). No change of the hydrogens relative to the carbons is assumed. Only the vibrations[2] $\nu_1 = 992$; $\nu_6 = 606$; $\nu_8 = 1596$ cm.$^{-1}$ are to be considered. Assuming that the angles of 120° are maintained, one obtains $\nu_1 = 5$; $\nu_6 = 0$; $\nu_8 = 10$. The high value of ν_8 is not in accord with the data. On the assumption that the C–C–C angle on the carbons 1 and 4 is equal to the tetrahedron angle, the values $\nu_1 = 5$, $\nu_6 = 2$, $\nu_8 = 3$ are obtained. Actually all bands can be represented by means of these frequencies, all except the first band by various combinations, too numerous to be listed here. The agreement gains more significance by the fact that only two frequencies are independent as accidentally $\nu_1 + \nu_6 = \nu_8$.

TABLE I

trans-DIBROMOETHYLENE $\nu_1 = 1578$; $\nu_2 = 1060$ cm.$^{-1}$

Band no.	1	2	3	4
$\nu_1\nu_2$	01	10	11	20
Calcd.	..	1578	2638	3156
Obs.	1060	1700	2600	3260

TABLE II

NAPHTHALENE, $\nu_1 = 1378$; $\nu_2 = 512$

Band no.	1	2	3	4	5	6
$\nu_1\nu_2$	01	10	11	20	30	40
Calcd.	512	1378	1890	2756	4134	5512
Obs.	500	1470	1880	2850	4250	5600

TABLE III

β-CHLORONAPHTHALENE, $\nu_1 = 1384$; $\nu_2 = 518$; $\nu_3 = 273$

No.	1	2	3	4	5	6	7	8	9	10
$\nu_1\nu_2\nu_3$	001	010	011	100	101	110	111	112	200	201
Calcd.	273	518	791	1384	1657	1900	2175	2448	2768	3041
Obs.	280	500	800	1320	1550	1810	2150	2350	2700	2900
No.		11	12	13	14	15	16	17	18	19
$\nu_1\nu_2\nu_3$		210	211	212	221	301	310	311	312	410
Calcd.		3286	3559	3804	4077	4425	4670	4943	5216	6054
Obs.		3170	3400	3600	3800	4300	4500	4700	5000	6000

A model in which the hydrogens 1 and 4 move out of the plane to occupy tetrahedron corners furnishes $\nu_5 = 10$; $\nu_{10} = 8$. The spectrum does not support this model.

Thus the somewhat more detailed, though still crude, application of the Franck–Condon principle confirms the quinoid model of Lewis and Kasha, and especially their assumption that the hydrogens do not appreciably move with respect to the carbons.

(3) Regarding the other substances investigated by Lewis and Kasha, vibration data are insufficient even for an approximate analysis. But the spectra of several substances can be safely correlated with two or three vibration frequencies. A few remarks are to be made on three of these substances.

The first frequency of *trans*-dibromoethylene (Table I) is well known as the stretching frequency of the ethylene bond. The second frequency has not been found among the five totally symmetric frequencies.[3] One is forced to conclude that the phosphorescent molecule has a lower symmetry than the symmetry C_{2h} of the ordinary molecule. If the assumption is made that the center of symmetry is maintained, the frequency 1060 must be correlated to the one frequency of the class B_g permitted in the Raman spectrum. This vibration consists essentially of an out-of-plane movement of the hydrogens.

Both Raman lines of naphthalene (Table II) are polarized; the vibrations therefore are totally symmetric.

The Raman frequencies of β-chloronaphthalene (Table III) have been taken from Magat's compilation.[4] A comparison with the spectra of the halogen derivatives of naphthalene indicates that the excited vibrations are not due to the halogen. The change of the aromatic bonds into double and single bonds seems to be the main cause of the distortion also in this case.

The authors are greatly indebted to Professor G. N. Lewis for advice and information.

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[2] *Cf.* E. B. Wilson, Jr., *Phys. Rev.*, **46**, 706 (1934); K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943).

[3] "Annual Tables of Constants and Numerical Data," vol. 11 (1931–1934), section 26, "Raman Effect" by M. Magat, Gauthier-Villars, Paris, 1936.

[4] Ref. 3, Vol. 12 (1935–1936), section 26, issue 15, Herman and Cie, Paris, 1937.

DEPARTMENT OF CHEMISTRY
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Chloromaleic Anhydride in the Diene Synthesis

BY MARTIN E. SYNERHOLM

The observation has been made that chloromaleic anhydride will react readily in a Diels–Alder condensation with propenyl phenols or phenol ethers[1] with loss of hydrogen chloride, yielding dihydronaphthalene derivatives. More tests have now been made in order to ascertain whether this addition–dehydrohalogenation is typical of the behavior of chloromaleic anhydride toward conjugated dienes. It is shown that the

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[1] Synerholm, THIS JOURNAL, **67**, 345 (1945).