The Absorption Spectrum and the Dissociation Energy of Fluorine

M. W. Nathans

Articles you may be interested in

Electronic Absorption Spectrum and Dissociation Energy of the Allyl Radical
J. Chem. Phys. **45**, 488 (1966); 10.1063/1.1727594

Absorption Spectrum and Dissociation Energy of the SO Radical
J. Chem. Phys. **37**, 1574 (1962); 10.1063/1.1733336

Erratum : Electronic Spectrum and Dissociation Energy of Fluorine
J. Chem. Phys. **27**, 1424 (1957); 10.1063/1.1744030

Electronic Spectrum and Dissociation Energy of Fluorine
J. Chem. Phys. **26**, 1567 (1957); 10.1063/1.1743583

Dissociation Energy of Fluorine
J. Chem. Phys. **24**, 1271 (1956); 10.1063/1.1742780

crystal patterns. The coordination scheme (number of nearest neighbors and interatomic distances) can be determined by a Fourier integral analysis[2] of the powder pattern, even when the pattern cannot be indexed and a complete structure determination is not possible.

The sample used in this investigation was boron of density 2.30 g/cm^{3} and of purity presumably greater than 99 percent. The crystalline form can be partially characterized by the prominent "d" values: 7.99, 5.52, 5.05, 4.69, 4.48, 3.57, 2.94, 2.86A. The Fourier analysis was made from the microphotometer record of a powder pattern made with crystal monochromated MoKα-radiation in a camera of diameter 8.93 cm. The area of the first peak of the radial distribution curve (Fig. 1) corresponds to 6.15 atoms. The area and position of this peak indicate six nearest neighbors at an average distance of 1.89A in crystalline boron.

[1] Laubengayer, Hurd, Newkirk, and Hoard, J. Am. Chem. Soc. 65, 1924 (1943).
[2] Hultgren, Gingrich, and Warren, J. Chem. Phys. 3, 351 (1935).

The Absorption Spectrum and the Dissociation Energy of Fluorine

M. W. Nathans*
Department of Chemistry, University of California, Berkeley, California
May 29, 1950

RECENT spectroscopic and thermal data on the heats of formation and dissociation of ClF[1] have cast doubt upon the value of 60 kcal. of the heat of dissociation, D_0, of F_2. The indications are that $D_0 = 30-40$ kcal. Pitzer[2] more or less arbitrarily assumed a tentative value of 50 kcal.

Wicke[3] has questioned the interpretation of the absorption spectrum of ClF, suggesting that the low intensity of the bands are not in agreement with the Franck-Condon principle. He also measured the thermal conductivity of fluorine as a function of the temperature and found it to agree with the conductivity of nitrogen. Since his calculated curves for F_2 and N_2 almost coincide if no dissociation occurs, Wicke concluded that his experiments supported a high dissociation energy. Finally, a low D_0 of F_2 would correspond to an electron affinity of fluorine which would be below that of chlorine.

These arguments are not conclusive.

1. If the interpretation of the absorption spectrum of ClF is wrong, the true D_0 of ClF could only be lower than the one obtained from spectroscopic data. This would lower the dissociation energy of fluorine, rather than increase it.

2. In the calculations of the heat conductivity a value for the collision cross section and for the vibrational frequency occurring in the specific heat had to be assumed. For the latter the value 856 cm^{-1} was calculated by Murphy and Vance with Badger's rule and the values for the other halogens and the interatomic distance.[4] Recently Andrychuk[5] obtained the Raman spectrum of fluorine and found the value 892 cm^{-1}. The difference with the assumed value will have only a small effect on the calculated heat conductivity.

More serious is the assumption that the collision cross section of F_2 lies between that of O_2 and of N_2, although the interatomic distance is larger than either of the two, viz., 1.48A as compared to 1.10A for N_2 and 1.21 for O_2. Using the values given by Pauling,[6] for the van der Waals radii of oxygen, nitrogen and fluorine, one finds the largest dimension of the diatomic molecules to be: 4.01A for O_2, 4.10A for N_2 and 4.18A for F_2. The collision cross section at $T = \infty$ may be several percent, probably five-ten percent higher than assumed by Wicke. This would cause the calculated curve for F_2 to be ten percent or more below the curve for N_2. Since the experimental results for N_2 and F_2 coincide to within ±10 percent, the heat conductivity experiments conducted by Wicke are not at all conclusive.

The probability of a low D_0 for F_2 was reason to investigate the absorption spectrum of F_2 in the photographic infra-red. The visible region was investigated by Gale and Monk[7] who could not detect any absorption. The region covered by the present work extended from 7000A to 9600A.

The spectra were obtained in a Baird spectrograph with a 3m concave grating and photographed on Eastman I-N and (hypersensitized) I-M plates. The light source was a tungsten ribbon lamb. A Corning-3480 filter was placed in the light beam in order to cut out the blue, which would otherwise have shown up as a second-order spectrum. A 185-cm Pyrex tube was used as the absorption cell. The fluorine was introduced into the cell under a pressure of approximately one atmos.

The only absorption that could be detected was the forbidden oxygen band at 7600A and water absorption around 9000A, due to the long light path through air (7m). The detection of the oxygen band is evidence of the sensitivity of the method, and it may be concluded that there is no allowed transition for F_2 from the ground state to an attractive upper state in the region 7000–9600A. The sensitivity of the instrument toward detection of a possible weak continuous absorption resulting from a transition to a repulsive state is not as high, however, as that toward the detection of discrete absorption lines, because of the large dispersion (5.55A/mm). No definite conclusions can, therefore, be drawn about the dissociation energy of fluorine from this work.

The thermochemical work on ClF, however, as well as the large interatomic distance of fluorine presumably caused by outer shell repulsion, and the doubtfulness of the interpretation by Wicke of his thermal conductivity measurement, favor the low value of the dissociation energy of fluorine.

I would like to thank Professor L. Brewer for the many discussions on the subject and also for providing the fluorine; Professor F. A. Jenkins for the discussions, and Dr. C. Thurmond for his aid in building the transferring system for the fluorine.

* Present address: Institute of Engineering Research, University of California, Berkeley, California.
[1] See, e.g., R. L. Potter, J. Chem. Phys. 17, 957 (1949).
[2] K. S. Pitzer, J. Am. Chem. Soc. 70, 2140 (1948).
[3] E. Wicke, Zeits. f. Elektrochemie 53, 212 (1949).
[4] Murphy and Vance, J. Chem. Phys. 7, 208 (1939).
[5] D. Andrychuk, J. Chem. Phys. 18, 233 (1950).
[6] L. Pauling, Nature of Chemical Bond (Cornell University Press, Ithaca, New York, 1945) p. 188.
[7] Gale and Monk, Phys. Rev. 29, 211 (1927); Mulliken, Phys. Rev. 46, 549 (1934), footnote 12a.

The Ionization Potential of Cyclopropane of Electron Impact

F. H. Field and E. A. Hinkle
Department of Chemistry, University of Texas, Austin, Texas
May 29, 1950

WE have determined the ionization potential of cyclopropane by electron impact and find its value to be 10.14 ± 0.05 volts.

The measurements were made with a Westinghouse Type LV mass spectrometer using the vanishing current method.[1] The calibrating gas of known ionization potential and the cyclopropane were introduced simultaneously. The potential normally used to move the ions from the region in which they are formed through the slit in the first ion-accelerating electrode (the ion-drawout or pusher potential) was maintained at zero in order to obtain a satisfactory degree of reproducibility of results. The sensitivity of the instrument was thus diminished, but the energy spread of the ionizing electrons was also diminished. The voltage of the ionizing electrons was measured by means of a voltage divider placed across the electrodes of the electron gun and a Leeds and Northrup Type K-2 potentiometer. The accuracy of the voltage

TABLE I.

Substance	Ionization potentials (volts)	
	Found	Literature
A	Pri. Std.	15.77[a]
N_2	15.60±0.06[b]	15.58[a]
CO_2	13.87±0.03	13.79,[c] 13.85[d]
CS_2	10.06±0.07	10.027,[e] 10.3[f]
C_3H_6[g]	10.14±0.05	
C_3H_6[h]	10.13±0.05	

[a] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, New York, 1932).
[b] All uncertainties calculated by multiplying the standard absolute errors by a factor which gives odds of 19 to 1 that the true mean lies within the resultant limits. See G. W. Snedecor, *Statistical Methods* (The Iowa State College Press, Ames, 1946), p. 65.
[c] Spectroscopic value. W. C. Price and D. M. Simpson, Proc. Roy. Soc. **A169**, 501 (1939).
[d] Electron impact value. R. E. Hornig, J. Chem. Phys. **16**, 105 (1948).
[e] Spectroscopic value. W. C. Price and D. M. Simpson, Proc. Roy. Soc. **A168**, 272 (1938).
[f] Electron impact value. T. M. Sugden and W. C. Price, Trans. Faraday Soc. **44**, 109 (1948).
[g] CO_2 used as secondary standard.
[h] CS_2 used as secondary standard.

measurements was greater than 0.1 percent. The temperature of the ionization chamber was maintained at 213±3°C.

Argon was used as the primary standard in calibrating the voltage scale. Unfortunately, the mass spectrum of cyclopropane[2] contains a contribution at mass 40, which prevented the direct use of argon as the calibrating gas in the determination of the cyclopropane ionization potential, but satisfactory results were obtained using carbon dioxide and carbon disulfide as secondary standards. The ionization potentials of these compounds were measured against argon.

The mass 42 peak of cyclopropane was symmetrical with no shoulders, and the peak height was a linear function of the pressure over the pressure range involved in the ionization potential determinations.

The cyclopropane, carbon dioxide, and argon were obtained from the Matheson Company and were used without further purification. The minimum purity given by the manufacturer for any of these substances was 99.5 percent. Commercial grade carbon disulfide was twice distilled through a packed column at a high reflux ratio, but the ionization potential was not altered by the purification.

Ten determinations of the ionization potentials of carbon disulfide and cyclopropane and thirteen determinations of the ionization potential of carbon dioxide were made. In general five separate samples were used, duplicate determinations being made on each. The results are summarized in Table I. The results of some measurements on nitrogen are also included in Table I. The good agreement of the ionization potentials of carbon dioxide, carbon disulfide, and nitrogen with previously reported values constitutes a check on the accuracy of the apparatus and method.

The ionization potential of cyclopropane can be compared with the values for propane (11.21 volts[3]), ethylene (10.62 volts by electron impace;[3] 10.50 volts by spectroscopic methods[4]), and propylene (9.84 volts by electron impact,[3] 9.6 volts by spectroscopic methods[4]). The ionization potentials of olefinic hydrocarbons are generally about a volt lower than those of the corresponding paraffinic compounds;[3] thus the ionization potential of cyclopropane indicates the presence of considerable unsaturation in this molecule. The value is compatible with Walsh's[5] concept of cyclopropane as a three-centered ethylene.

Using Walsh's model, Music and Matsen[6] calculated the wavelengths of the near ultraviolet spectrum of phenylcyclopropane, obtaining qualitative agreement with the observed values. It was assumed that the carbon π-bond Coulomb integrals are the same for all unsaturated hydrocarbons and that |β-cyclopropane| $\cong 0.9$|β-ethylene| where β is the resonance integral. On the basis of these assumptions and the further assumption that the ioniza-

tion potential of cyclopropane is given by $-(\alpha-\beta)$, the calculated ionization potential is lower than that of ethylene, which is in agreement with the experimental findings. Such agreement may be interpreted as evidence in favor of Walsh's model.

We should like to thank the Humble Oil and Refining Company of Baytown, Texas for the gift of the mass spectrometer.

[1] T. Mariner and W. Bleakney, Phys. Rev. **72**, 807 (1947).
[2] "Catalog of Mass Spectral Data," A.P.I. Project 44, Serial numbers 115, 172, and 181, National Bureau of Standards, Washington, D. C.
[3] R. E. Hornig, J. Chem. Phys. **16**, 105 (1948).
[4] W. C. Price and W. T. Tutte, Proc. Roy. Soc. **A174**, 207 (1940).
[5] A. D. Walsh, Trans. Faraday Soc. **45**, 179 (1949).
[6] J. F. Music and F. A. Matsen, J. Am. Chem. Soc. (to be published).

Remarks on a Paper by Riddell and Uhlenbeck

H. S. GREEN
Institute for Advanced Study, Princeton, New Jersey
May 1, 1950

PROFESSOR UHLENBECK has been kind enough to send me a copy of a manuscript by Mr. Riddell and himself,[1] already submitted for publication, in which reference is made to two other papers by de Boer[2] and myself.[3] As this contains a number of statements which appear to me inexact, I should welcome the opportunity to make the following comments.

As a preliminary remark, I do *not* consider that the thermodynamic and kinetic pressures are identical *only* in classical approximation, but also in a gas, where the surface energy is negligible, and in a liquid above a certain temperature. Further, neither de Boer nor myself introduces the complication of an external potential W into our considerations, for a reason which Riddell and Uhlenbeck appear to have overlooked. I affirm the following statements concerning their paper: (i) that, as a consequence of the inclusion of the potential term $W(q/L)$ in the Hamiltonian, the quantity p defined by Eqs. (4) and (5) is not the required thermodynamic pressure, *except* when the function $W(q/L)$ is infinite outside a region of volume $V = L^3$; (ii) that, when $W(q/L)$ has this character, Eq. (6) is incorrect; and (11) is also incorrect; and (iii) that, although (14) is correct, the considerations of Section 5 fail to justify the conclusion that the term containing μ_0 contributes to the pressure, but not the terms containing μ_1, μ_2, etc.

To prove the statement (i), it is sufficient to consider the classical limit. One sees immediately that the density of the fluid varies from place to place as $\exp{-\beta W(q/L)}$, and that in the classical limit the quantity p is given by

$$Vp = N/\beta + \tfrac{1}{3}\overline{\Phi}, \tag{a}$$

where $V = L^3$, N is the number of molecules, and $\overline{\Phi}$ is the total virial of the molecular forces for *the volume* V_1 occupied by the fluid. The two volumes V_1 and V are only identical if $W(q/L)$ is infinite outside a region of volume L^3. Only then, therefore, will p represent the thermodynamical pressure. If the pressure is to be unique, it is necessary also for $W(q/L)$ to vanish inside the volume V.

To prove the statement (ii), suppose that the function $W(q/L)$ is of the type required; then one may no longer use "the hermitian property of $\mathfrak{IC}$" to derive (6). For

$$\int \left\{ \Psi_n^* \left(\mathfrak{IC} \frac{\partial \Psi_n}{\partial L} \right) - (\mathfrak{IC}\Psi_n)^* \frac{\partial \Psi_n}{\partial L} \right\} d\tau$$

$$= -\frac{\hbar^2}{m} \Sigma_i \int \frac{\partial}{\partial q_i} \left\{ \Psi_n^* \frac{\partial^2 \Psi_n}{\partial q_i \partial L} - \frac{\partial \Psi_n^*}{\partial q_i} \frac{\partial \Psi_n}{\partial L} \right\} d\tau, \tag{b}$$

and, since $\partial \Psi_n / \partial q_i$ and $\partial \Psi_n / \partial L$ are both finite on the wall, however large the value of L, the surface integral arising from the second term cannot generally be discarded. One might attempt to remedy the argument in replacing $\mathfrak{IC}$ by $\exp{-\beta \mathfrak{IC}}$; this has been