tor impurity Y, ionization potential $y$. Let both a pure X lattice and an X lattice containing $y$ be ionized, the charge center being at a Y atom in the latter case. The difference in energies of these two states is simply $(x - y)$, and this represents the depth of the impurity level below the conduction band, since the first case corresponds to photoexcitation of the host. The transition from the valence band to the impurity level is permitted if $x - y$ is positive, and we can thus derive the following results for heavily doped Ni-based diamond (Table II). These calculations are confirmed by the results of several hundred experiments in these systems, though the nearest we have come to a true red diamond is a russet-brown hue by Be-doping or by very heavy doping with B, Al, and Si combined. The results here are doubtless complicated by the possibility of multiple ionization processes. The anticipated effect of Si alone in

TABLE II

SINGLE BOND-ENERGY CALCULATION FOR IMPURITIES IN DIAMOND

|  | $x$ | $y$ | $x - y$ | $5.2 - (x - y)$ | Absorption | Crystal color | Color obsd. |
|---|---|---|---|---|---|---|---|
| X = C, Y = B | 11.26 | 8.30 | 2.96 | 2.2 | Red | Blue | Blue |
| Al | 11.26 | 5.98 | 5.29 |  | Infrared | None | None |
| Be | 11.26 | 9.32 | 1.94 | 3.3 | Blue | Red | Russet |

small quantities would be to give absorption in the near-red; this may be the cause of some of the more desirable colors of natural diamond. The same is true of calcium, which is also found as a frequent trace impurity in natural stones. Qualitative agreement with these latter predictions has been observed, as described. A more sophisticated treatment should take some account of the possibility of compensated nitrogen centers[7] affecting the absorption.

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# The Determination of the Geometry of High-Temperature Species by Electric Deflection and Mass Spectrometric Detection[1a]

BY ALFRED BÜCHLER,[1b] JAMES L. STAUFFER,[1b] AND WILLIAM KLEMPERER[1c]

The electric deflection of mass spectrometrically detected molecular beams has been used to study the molecular geometry of high temperature species by determining whether they possess permanent dipole moments or not. By this means it has been shown that (1) the lithium halide dimers are planar; (2) lithium oxide, $Li_2O$, is linear; (3) the beryllium and magnesium dihalides are linear; the barium dihalides are bent; (4) the group IIB dihalides are linear; (5) the dihalides of the transition metals from manganese through copper are linear; (6) the lead dihalides are bent. Both PbI and $PbI_2$ were found in lead iodide vapor. Many of the structural results are in disagreement with the prediction of simple theories of molecular geometry.

The importance of the electric dipole moment in molecular structure determination is well known.[2,3] Today there exist several experimental techniques for determining molecular structures which were unavailable as recently as 20 years ago and which are capable of very high precision and reliability. Crude structural determinations by means of electric polarity might therefore be regarded as retrogressive. In one area, however, the chemistry of high temperature systems involving polyatomic species, sophisticated spectroscopic methods have been difficult to apply, and a return to earlier techniques therefore appears to be useful.

The probable complexity of the vaporization of simple inorganic compounds was first stressed by Brewer. He pointed out that the complexity of the saturated vapors would most likely increase with increasing temperature, since the entropy $(-T\Delta S)$ term of the free energy would eventually overwhelm any unfavorable enthalpy $(\Delta H)$ value. Since Brewer and Lofgren's pioneering work on the vaporization of cuprous chloride[4] in which the existence of $Cu_3Cl_3$

was demonstrated, a large number of polyatomic molecules have been shown to exist in saturated vapors at all temperatures investigated, i.e., to approximately $3000°K$. These species have been identified principally by mass spectrometric analysis of the vapors.[5] The variety of species which have been found in this way is well illustrated by a list of gaseous polyatomic alkali compounds. The 1959 review cited[5] lists halides,[6] oxides,[7] and hydroxides.[8] Since that time, gaseous alkali cyanides,[9] metaborates,[10] nitrates,[11] and molybdates,[12] as well as mixed alkali-beryllium,[13] alkali-aluminum,[14] and alkali-transition metal halides,[13,15] have been shown to exist.[16]

(1) (a) This paper was intended for the issue of this journal honoring Professor P. Debye on his 80th birthday. This research was sponsored by the Advanced Research Projects Agency, U. S. Department of Defense, under Contract DA-19-020-ORD-5584, ARPA Order No. 40-62, monitored by U. S. Army Research Office; (b) Arthur D. Little, Inc.; (c) Harvard University; Consultant, Arthur D. Little, Inc.

(2) (a) "Dipolmomente und Chemische Struktur," Leipziger Vorträge 1929, P. Debye, Ed., S. Hirzel, Leipzig, 1929; (b) P. Debye, "Polar Molecules," Dover Publications, New York, N. Y., 1929 and 1945.

(3) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.
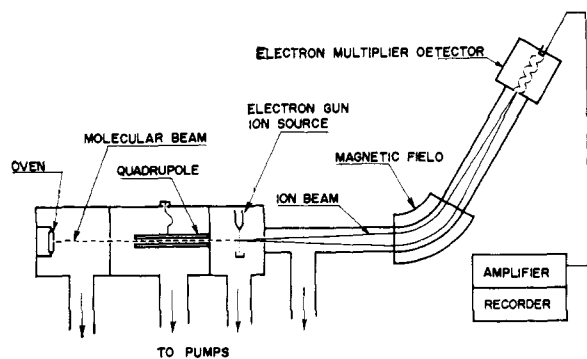
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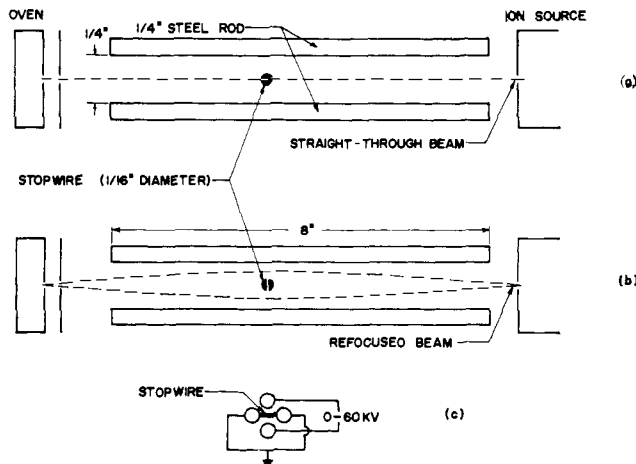
Fig. 1.—Schematic diagram of the apparatus.



Fig. 2.—Operation of the quadrupole field: (a) straight-through beam measurement (quadrupole field off); (b) refocused beam measurement (quadrupole field on).

An attack on the structure of polyatomic species at high temperatures may proceed by several routes. Pure rotational spectroscopy, which is certainly the ideal method for polar species, suffers from two disadvantages. The first problem appears to be an instrumental one, namely, the construction of a high-sensitivity microwave spectrometer capable of high-temperature operation. Those spectrometers which have been successful[17,18] appear to have a sensitivity of about three orders of magnitude below the usual room temperature spectrometer. Secondly, since the molecular partition function is large at high temperatures for species with relatively low-frequency vibrations and since the microwave spectrometer generally resolves rotational transitions of different vibrational states, the intensity of the individual lines is expected to be low. So far it appears that no polyatomic high temperature species has been successfully studied by microwave absorption spectroscopy.

Electron diffraction has been used in a relatively large number of instances for the structural study of polyatomic high temperature species. In general, the large thermal amplitude of internal coordinates results in a diffraction pattern which has a lower resolution than obtains with gases at low temperatures. Frequently some interatomic distances (particularly those involving nonbonded atoms) cannot be obtained with any appreciable reliability. An example is provided by the careful study of lithium chloride dimer, $Li_2Cl_2$, by Bauer, Ino, and Porter.[19] Here the Li–Cl and Cl–Cl distances were obtained. The Li–Li distance, however, which would have been needed to settle the question of the planarity of the ring, could not be observed because of the intrinsic weakness of coherent scattering corresponding to it and the breadth of the other features in the pattern. Similarly, in Akishin and Spiridonov's study of the group II dihalides[20] the metal–halogen distances could be determined with good precision, but large uncertainties in the bond angle were stated by these authors as a result of the difficulty of determining the halogen-halogen distances. In these two instances it is obvious that whether the species in question is polar or not is important in determining its structure.

The molecular beam electric deflection technique was demonstrated and used by Kallman and Reiche,[21]

Stern,[22] Estermann,[23] and many others.[24] The relative ease and reliability of detection of molecular beams by the modern mass spectrometer has been amply demonstrated by Inghram, Chupka, and their associates in the study of high temperature systems. It is well to point out that the question of what species are present and are being examined in high temperature molecular beam experiments is frequently quite subtle. It is therefore of considerable advantage to use as detector a mass spectrometer of good resolution with an electron bombardment ion source. The combination of an electric quadrupole deflecting field[25,26] and a mass spectrometer of the type described permits the rapid examination of a number of molecular systems for the purpose of determining whether they have permanent dipole moments or not. The results of such a study are presented in this paper.

### Experimental

The apparatus used is sketched in Fig. 1. It consists essentially of a Knudsen effusion source for producing the molecular beam, an electric quadrupole field which deflects it, and a mass spectrometer which measures its intensity. A detailed sketch of oven and quadrupole assembly has been given in a recent publication.[27] In most experiments, the source oven consists of a small platinum or tantalum tube 0.95 cm. in diameter with a 0.0076-cm. diameter effusion orifice. These and the following dimensions, when converted to English units, will be found to correspond to standard machine shop sizes. The tube is heated by passing a large electric current through it. The quadrupole is 20.3 cm. long and consists of four well-polished 0.635-cm. stainless steel rods. The rods are insulated from each other by being mounted on the inside of a pair of sapphire rings. Two of the rods are at ground potential and serve to hold a stop wire (see below) and the mounting bracket. The highest voltages reached before electrical breakdown occurred have been in the vicinity of 40 kv. The mass spectrometer used in these experiments is a Nuclide Corporation 30.48-cm. radius, 60° sector magnetic deflection instrument designed by Inghram. Molecules entering the ion source of the mass spectrometer from the quadrupole chamber are ionized by 70-v. electrons. The ions formed are accelerated by a 4000-v. field, mass analyzed by a magnetic field, and detected by an electron multiplier.

The operation of the quadrupole field is shown in Fig. 2, and

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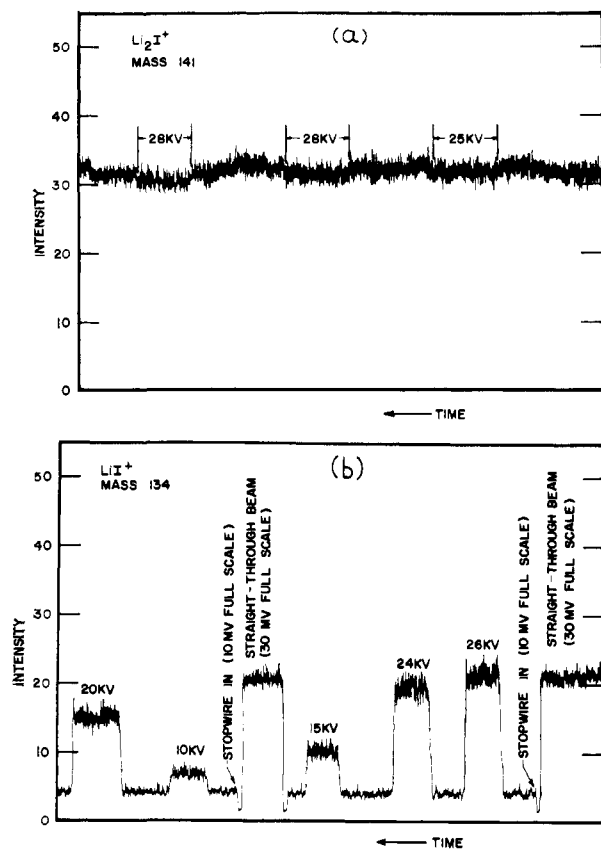
Fig. 3.—Mass spectrometer traces: (a) refocusing of LiI beam; (b) defocusing of straight-through $Li_2I_2$ beam. The voltages indicated on the traces are those applied to the quadrupole.

the resulting traces illustrated in Fig. 3. The stopwire, which is located near the center of the quadrupole field, is slotted, so that initially (with the quadrupole field turned off) the gas source may be put on a straight line determined by the stopwire (i.e., axis of quadrupole) and the detector (the detector here being the entrance slit of the mass spectrometer ion source), and the straight-through beam intensity measured (Fig. 2a). The stopwire is then rotated 90°. In this position the stopwire casts a shadow of the beam source on the detector and optically stops the beam (a small signal, approximately 0.5% of the straight-through beam, is still observed under these conditions, presumably due to scattering of beam molecules by residual gas). When the electric field is turned on, polar molecules in certain rotational states will be deflected in the direction of lower electric field strength. These molecules may thus take curved paths around the stopwire and be refocused onto the entrance slit of the mass spectrometer (Fig. 2b). The refocusing of lithium iodide monomer, LiI, is shown in Fig. 3a.[28] No such effect will be observed for nonpolar molecules. The latter will be defocused by the quadrupole field, an effect which can be seen in the case of molecules of high polarizability, such as lithium iodide dimer, $Li_2I_2$. Here $Li_2I^+$ shows defocusing when the electric field is turned on while the straight-through beam is being examined (Fig. 3b).

## Results

The new results obtained are summarized in Table I. For the sake of completeness, some results on group II compounds presented earlier[27] have also been included. Individual groups of molecules will be discussed below. The effective sample temperatures at which the experiments were carried out were such as to correspond to vapor pressures of the order of $10^{-3}$ to $10^{-4}$ atm. Unless otherwise indicated, straight-through beam intensities refer to the most abundant isotopic

species present. The refocused beam intensity is given as a percentage of straight-through beam intensity; because of the relatively narrow aperture of the system for the straight-through beam, more than 100% refocusing was observed in at least one case. In those cases where refocusing does not occur, the sensitivity of the experiment is shown in terms of the minimum amount of refocusing (again expressed as a percentage of straight-through beam) which could have been detected. In some instances, both refocusing and nonrefocusing species contribute to a given ion current; for example, in lithium iodide, the $Li^+$ ion current contains contributions from the dissociative ionization of both LiI and $Li_2I_2$. In these cases, only the refocusing (and hence polar) species is shown in the last column of Table I.

**Group IA. Lithium Halide Dimers.**—The lithium halide dimers have generally been assumed to have planar rhombic configurations. Two electron diffraction studies have been carried out,[19,29] but failed, for the reasons discussed earlier in this paper, to provide the evidence required to establish the planarity of these molecules. Refocusing data for the four lithium halides are shown in Table I. Data for lithium fluoride and lithium chloride were obtained with an earlier version of the apparatus, while the lithium bromide and lithium iodide data were obtained with the present system, which has a sixfold increase in sensitivity over the older equipment. The examination of lithium iodide dimer constitutes the most critical experiment since this molecule provides the most obvious case in which ionic considerations would lead to the prediction of deviations from planarity, with the nonplanar structure stabilized by the dipoles induced in the highly polarizable iodide ions. The refocused signal observed in the case of the $Li^+$ and $LiX^+$ ions is due to the polar monomers LiX, with dipole moments 6.3,[30] 7.1,[18] 6.2,[17] and 6.3[17] D., respectively, for LiF, LiCl, LiBr, and LiI. The absence of refocused signal in the case of $Li_2F^+$, $Li_2Cl^+$, and $Li_2Br^+$, and even more strongly, the defocusing of the beam seen in the case of $Li_2I^+$ (Fig. 3b) demonstrate the lack of polarity of the lithium halide dimers and show that these molecules are indeed planar.

**Lithium Oxide.**—A study of lithium oxide has already been presented in a previous publication.[12] Deflection measurements showed a linear structure for $Li_2O(g)$ and also showed the presence of diatomic LiO in the equilibrium vapor. The lithium oxide system was re-examined with the present more sensitive equipment; the data obtained are shown in Table I. Lack of refocusing was again observed for $Li_2O$, confirming its lack of polarity and hence its linearity.

**Group IIA. Beryllium and Magnesium Halides.**— Refocusing of the alkaline earth dihalides by inhomogeneous electric fields was first reported by Wharton, Berg, and Klemperer (WBK),[31] who demonstrated that many of these compounds are nonlinear. Because of the use of a Langmuir–Taylor surface ionizer as beam detector, these experiments could not by themselves establish the actual species which contained

(28) The statement that an ion $M^+$ shows refocusing (or, less accurately, that $M^+$ is refocused) always implies that a *neutral precursor* of $M^+$ is refocused by the quadrupole field, and that this refocusing is detected by means of the behavior of the $M^+$ ion current intensity.

(29) P. A. Akishin and N. G. Rambidi, *Zh. Neorgan. Khim.*, **3**, 2599 (1958); *Z. physik. Chem.*, **213**, 111 (1960).

(30) L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, *J. Chem. Phys.*, **38**, 1203 (1963).

(31) L. Wharton, R. A. Berg, and W. Klemperer, *ibid.*, **39**, 2023 (1963).

the metal. (Further magnetic deflection studies in the case of barium dichloride showed that the species $BaCl_2$ was indeed the polar species.) In addition, the high ionization potentials of Be and Mg preclude the efficient detection of their halides. In the present apparatus beryllium fluoride and chloride and magnesium fluoride showed no evidence of nonlinearity (Table I). In the case of the beryllium compounds an attempt was made to find evidence for the presence of diatomic species through the addition of a reducing agent, the systems chosen being those studied by Hildenbrand, Theard, and Ju.[32] For both BeF and BeCl sensitivity was low because of background peaks in the mass spectrum. In addition the polarity of BeF and BeCl may not be very large. The assignment of the three outer electrons to the orbitals $(Be_{s+p\sigma} + F_{p\sigma})^2(Be_{s-p\sigma})$ leads to an expected dipole moment near 2 D. The absence of refocusing, although not as strong evidence for vapor composition as might be desired, is in agreement with the conclusions of Hildenbrand, et al., who found no significant amount of monohalides in these systems. In the beryllium fluoride experiment, diatomic AlF was formed by reaction of $BeF_2$ with the aluminum present and was observed to refocus. The dipole moment of AlF has been measured by Lide[33] to be 1.4 D.

For magnesium fluoride, no refocusing of the triatomic parent ion $MgF_2^+$ was observed, indicating within our sensitivity that $MgF_2$ is nonpolar and therefore linear. The fragment ion $MgF^+$ also remained unrefocused as long as a platinum oven was used to contain the sample. In a tantalum oven, however, refocusing of $MgF^+$ was observed, while $MgF_2^+$ remained unrefocused.[34] This result clearly establishes the presence of diatomic MgF in the vapor under reducing conditions.

**Calcium and Barium Halides.**—Data for calcium fluoride and barium fluoride have already been presented.[27] These molecules span the range from highest to lowest polarities found by WBK.[31] These authors, using a surface ionization detector, established that the electrically refocused species in the alkaline earth halides was the dihalide by a study of the *magnetic* deflection of the molecular beams in the barium chloride system. For $CaF_2$ and $BaF_2$ no parent ion $MX_2^+$ is produced by electron bombardment ionization, but refocusing of the diatomic fragment ions $CaF^+$ and $BaF^+$ was found. Barium iodide was examined in the hope (based on the results of Berkowitz and Marquart[35] for the magnesium halides) that a stable parent ion might exist. $BaI_2^+$ was in fact observed and found to show refocusing. This result confirms once again, and in a very satisfying fashion, the conclusion of WBK that all barium halides are bent.

It may be noticed that the percentage of refocusing of $BaI^+$ is less than that of $BaI_2^+$. Our somewhat speculative conclusion at this time is that BaI is present

in the vapor and that it refocuses to a lesser extent than $BaI_2$. Because of the fragmentation of the latter, however, quantitative statements are difficult.

**Group IIB Halides.**—Data for the three fluorides, zinc and mercuric chloride, and mercuric iodide are given in Table I. Mercuric chloride, bromide, and iodide are the only group II dihalides for which adequate spectroscopic evidence exists[36]; this evidence indicates that they are linear. In addition, a microwave study[37] of $CH_3HgCl$ and $CH_3HgBr$ showed these related compounds to be linear. Mercuric chloride and mercuric iodide were examined since it had been suggested that, for molecules with very low bending force constants ($HgCl_2$ has a bending frequency of 70 cm.$^{-1}$, $HgI_2$ one of 35 cm.$^{-1}$), excited vibrational states might act as nonlinear molecules and show refocusing. In point of fact defocusing was observed in the case of $HgCl_2$, in accord with the expected behavior of a linear molecule. For $HgI_2$ the sensitivity of the experiment was low because of a very large scattered beam background; within this sensitivity, no refocusing was observed.

Ionic model calculations which predict nonlinearity for group IIA halides also tend to predict nonlinearity for the mercuric halides. Such ionic effects should be strongest in mercuric fluoride,[38,39] which was therefore examined. No refocusing was observed, showing that mercuric fluoride also is linear. The linearity of $ZnF_2$ was demonstrated earlier.[27] Cadmium fluoride was examined since it is known[39] that other properties of the group IIB dihalides (e.g., bond lengths and stretching force constants) do not vary monotonically on going from zinc to mercury; it, too, was found to be nonpolar and therefore linear. Since, therefore, all group IIB fluorides, as well as the dichloride, dibromide, and diiodide of mercury, have now shown to be linear, it is reasonable to conclude that, in accord with electron diffraction studies,[20] all group IIB dihalides are linear.

**Group IV Halides.**—Refocusing data for lead chloride and lead iodide[40] are shown in Table I. An early electron diffraction study[41] interpreted the tin and lead dihalides as being bent, with a bond angle of 95°. Repetition of this work[42] with more sensitive equipment and reanalysis of the earlier data showed that only the lead–halogen bond distance could be determined, the angle remaining in doubt. Akishin and his associates were in fact led to question[42] the very existence of the triatomic halides in the vapor. The present results show both the existence of these compounds and their nonlinearity. In addition, the amounts of refocusing of $PbCl_2^+$ and $PbCl^+$ are identical within the limits of experimental error, thus showing neutral $PbCl_2$ to be the precursor of both ions. The amount of refocusing shown by $PbI^+$ is several times that of $PbI_2^+$, showing that in the case of the iodide the vapor contains diatomic PbI as well as $PbI_2$.

(32) D. L. Hildenbrand, L. P. Theard, and F. Ju, Aeronutronic Publication U-2116, Contract No. AF 04(611)-8523, April 30, 1963, p. 19.

(33) D. R. Lide, Jr., *J. Chem. Phys.*, **38**, 2027 (1963).

(34) The data of Table I show a smaller $MgF^+$–$MgF_2^+$ ratio when $MgF(g)$ was present in the vapor than when it was not. This apparent paradox is thought to be due to a change in ion source conditions and hence in the observed $MgF_2$ fragmentation pattern as a result of work on the source between the two sets of experiments.

(35) J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, **37**, 1853 (1962).

(36) See W. Klemperer and L. Lindeman, *ibid.*, **25**, 397 (1956), for a discussion of the spectroscopic studies.

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(39) A. Büchler, W. Klemperer, and A. G. Emslie, *ibid.*, **36**, 2499 (1962).

(40) We are obliged to Dr. D. Cubicciotti for drawing our attention to these compounds.

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TABLE I

ELECTRIC DEFLECTION EXPERIMENTS

| System | Ion | Mass | Straight-through beam | % refocused | % sensitivity | Species Polar | Nonpolar |
|---|---|---|---|---|---|---|---|
| | | | | Group I | | | |
| LiF | Li⁻ | 7 | 0.24 | 0.54 at 30 kv. | | LiF | |
| | LiF⁺ | 26 | 0.11 | 2 at 30 kv. | | LiF | |
| | Li₂F⁺ | 33 | 0.18 | 0 | 0.057 | | Li₂F₂ |
| LiCl | Li⁺ | 7 | 0.10 | 0.51 at 25 kv. | | LiCl | |
| | LiCl⁻ | 42 | 0.15 | 2.9 at 25 kv. | | LiCl | |
| | Li₂Cl⁺ | 49 | 0.23 | 0 | 0.09 | | Li₂Cl₂ |
| LiBr | Li⁺ | 7 | 0.31 | 4.7 at 25 kv. | | LiBr | |
| | LiBr⁺ | 86 | 0.23 | 11 at 24 kv. | | LiBr | |
| | Li₂Br⁻ | 93 | 0.37 | 0 | 0.8 | | Li₂Br₂ |
| LiI | Li⁺ | 7 | 0.38 | 9 at 28 kv. | | LiI | |
| | LiI⁺ | 134 | 0.58 | 35 at 29 kv. | | LiI | |
| | Li₂I⁻ | 141 | 0.9 | Defocused | | | Li₂I₂ |
| Li₂O | | | | | | | |
| (1210°) | LiO⁺ | 23 | 0.11 | 50 at 33 kv. | | LiO | |
| (1270°) | Li₂O⁻ | 30 | 26 | 0 | 0.35 | | Li₂O |
| | | | | Group IIA | | | |
| BeF₂ + Al | BeF⁺ | 28 | 17 | 0 | 3 | | BeF₂ |
| | BeF₂⁻ | 47 | 45 | 0 | 0.2 | | BeF₂ |
| | AlF⁻ | 46 | 16 | 0.4 at 32 kv. | | AlF | |
| BeCl₂ + W | BeCl⁺ | 46 | 0.9 | 0 | 2 | | BeCl₂ |
| | BeCl₂⁺ | 79 | 22 | 0 | 0.2 | | BeCl₂ |
| MgF₂ | MgF⁺ | 43 | 14 | 0.7 at 24 kv. | | MgF | |
| (Ta oven) | MgF₂⁻ | 62 | 4.5 | 0 | 0.4 | | MgF₂ |
| MgF₂ | MgF⁻ | 43 | 4.2 | 0 | 0.4 | | MgF₂ |
| (Pt oven) | MgF₂⁺ | 62 | 0.57 | | | | MgF₂ |
| CaF₂ | CaF⁺ | 59 | 0.54 | 0.44 at 22 kv. | | CaF₂ | |
| BaF₂ | Ba⁺ | 138 | 1.7 | 6.0 at 27 kv. | | BaF₂ | |
| | BaF⁻ | 157 | 7.3 | 5.5 at 27 kv. | | BaF₂ | |
| BaI₂ | BaI⁺ | 265 | 0.51 | 1.8 at 28 kv. | | BaI₂, BaI | |
| | BaI₂⁺ | 392 | 0.48 | 4.2 at 28 kv. | | BaI₂ | |
| | | | | Group IIB | | | |
| ZnF₂ | Zn⁻ | 64 | 11 | 0 | 0.4 | | ZnF₂ |
| | ZnF⁺ | 83 | 64 | 0 | 0.15 | | ZnF₂ |
| | ZnF₂⁺ | 104 | 45 | 0 | 0.2 | | ZnF₂ |
| ZnCl₂ | ZnCl⁻ | 103 | 0.012 | 0 | 4 | | ZnCl₂ |
| | ZnCl₂⁺ | 134 | 0.40 | 0 | 0.25 | | ZnCl₂ |
| CdF₂ | Cd⁺ | 114 | 1.7 | 0 | 1.8 | | CdF₂ |
| | CdF⁺ | 133 | 2.4 | 0 | 0.6 | | CdF₂ |
| HgF₂ | HgF⁺ | 221 | 12 | 0 | 0.8 | | HgF₂ |
| | HgF₂⁻ | 240 | 8.4 | 0 | 1.1 | | HgF₂ |
| HgCl₂ | HgCl⁺ | 272 | 2.1 | Defocused | | | HgCl₂ |
| HgI₂ | HgI₂⁺ | 456 | 1.2 | 0 | 12 | | HgI₂ |
| | | | | Group IV | | | |
| PbCl₂ | PbCl⁺ | 243 | 0.48 | 7.1 at 20 kv. | | PbCl₂ | |
| | PbCl₂⁺ | 278 | 0.37 | 11 at 24 kv. | | PbCl₂ | |
| PbI₂ | PbI⁺ | 335 | 0.47 | 130 at 24 kv. | | PbI₂, PbI | |
| (Pt oven) | PbI₂⁻ | 462 | 0.52 | 33 at 24 kv. | | PbI₂ | |

## Discussion

**Alkali Halide Dimers.**—The present investigation shows that all of the lithium halide dimers are nonpolar molecules. This, together with the electron diffraction studies,[19,29] implies either a planar centrosymmetric structure, or, at worst, a nonplanar structure with a very high inversion frequency and there-fore low barrier to tunneling. In view of the observation that *all* of the lithium halide dimers are nonpolar it seems likely that the common explanation of nonpolarity because of planar equilibrium geometry is correct. The question of the geometric structure of the lithium halide dimers is then considered complete, the symmetry being $D_{2h}$ and the Li–X and X–X

distances being those given by electron diffraction studies for X = Cl, Br, I.

A point should be made concerning the distances observed in the lithium halide dimers. The Li–Li distance varies slightly from 2.64 Å. in $Li_2Cl_2$ to 2.75 Å. in $Li_2I_2$. These distances are considerably shorter than the Li–Li distance in metallic lithium (3.04-Å. high temperature phase)[43] and is effectively equal to the Li–Li bond length in diatomic $Li_2$ (2.67 Å.).[43] It is seen that the usual argument which associates a short metal–metal bond length with chemical bonding does not work in this case, since it seems reasonable to assume that there is no direct chemical bond between the two lithium atoms in the lithium halide dimers.

**$XY_2$ Molecules.**—The majority of molecular species investigated in this and previous[12,27] reports are symmetrical triatomic molecules, in which the problem of interest is the apex angle. The results may be summarized as follows. (1) The group IIA halides are linear or bent, depending on the specific metal–halogen combination. A bent configuration is favored by the combination of heavy metal atoms and light halogens. All barium halides are nonlinear; whereas, among the calcium halides only the fluoride is bent. No evidence of nonlinearity was found for $MgF_2$ and $BeF_2$. (2) The group IIB halides are linear. (3) The dihalides of the transition metals between manganese and copper are bent.[27] (4) The lead halides are bent.

The question as to whether a given triatomic molecule is linear or bent is certainly among the simplest problems in polyatomic geometry. It is seen in Table I that, as found in previous work, the percentage of beam refocused is large for several of the polar species, and that therefore the electric dipole moment and angular deviation from linearity are large. The angle in $BaF_2$ was estimated by WBK[31] to be approximately 120°.

A number of qualitative conclusions may be drawn from the experimental observations. The coarse geometry of a symmetrical triatomic molecule $XY_2$ is not determined by the central atom X alone. This has already been seen in the strontium halides where the fluoride and chloride are polar and the bromide and iodide are nonpolar. Similarly, for $OY_2$ compounds the bond angle changes from 180° for $Li_2O$[12,44] through 145° for $(SiH_3)_2O$[45] to 105° for $H_2O$.[43] For both $OY_2$ and $SrY_2$ it seems highly probable that any angle between 100 and 180° may be found by a proper choice of Y; it is apparent also, from the example of the $OY_2$ compound, that this behavior does not depend at all on steric effects. In group IV, the divalent carbon compounds provide a third set of molecules, the geometry of whose electronic ground state is not solely determined by the central atom. The ground state of $CH_2$ is linear $^3\Sigma$, the nonlinear $^1A$ state lying above it.[46,47] For $CF_2$ spectroscopic evidence[48] indicates a nonlinear ground state. The divalent silicon com-

pounds which have been examined spectroscopically, $SiHCl$,[47] $SiHBr$,[47] and $SiF_2$,[49] have all been found to be bent. For SiHCl and SiHBr, the position of the $^3\Sigma$ and $^1A$ levels is the reverse of that in $CH_2$.[47] Here both configurations are bent; the bond angle in the excited $^3\Sigma$ is, however, significantly more open than that in the ground $^1A$ state. The present work on $PbCl_2$ and $PbI_2$ and the spectroscopic data for $CF_2$[48] and $SiF_2$[49] indicate that all group IV dihalides are bent. No data are available for $SiH_2$ or any carbon hydrohalides CHY; such data would be of considerable interest, since they would provide evidence as to the relative degree in which central atom and ligands affect the ground-state geometry of group IV compounds.

It has been seen that the central atom X does not determine the geometry of a symmetrical molecule $XY_2$. In a related manner, for a fixed terminal group Y, the geometry of $XY_2$ is not solely determined by the column of the periodic table in which X is located. This is well illustrated by the difluorides of the alkaline earths. $BaF_2$ and $SrF_2$ are highly polar, while $MgF_2$ and $BeF_2$ are nonpolar. Evidently the number and configuration of the valence electrons in an atom do not determine the geometric behavior of its dihalides. There is a striking difference in geometry between the dihalides of group IIA and IIB. All of the IIB dihalides are linear, including $HgF_2$.

To account for the results just discussed, two models of chemical bonding can be presented, each of which has in the past proved useful in correlating a number of observations even though neither has a serious claim toward being rigorous or even being a first approximation to a rigorous model. These are the ionic model and the directed valence model based on valence-state arguments. If the behavior of the alkaline earths is correlated with an ionic model, the potential function for the bending motion is quite sensitive to the value of the metal ion polarizability. This may be seen by examining the behavior of the Rittner model potential functions for the group II halides presented earlier.[39] Typically, if the polarizability of $Ba^{+2}$ is 3.5 Å.,[3] all of the species $BaX_2$ have a bent equilibrium geometry. For $SrX_2$ it is necessary to carefully choose $Sr^{+2}$ = 2.25 Å.[3] in order to obtain a bent $SrF_2$ and $SrCl_2$ while keeping $SrBr_2$ and $SrI_2$ linear. While this does produce the observed geometric pattern, the potential function seems much too flat. In $SrCl_2$ the equilibrium angle calculated is 135°, but the minimum is only 100 cm.$^{-1}$ below the energy of the linear configuration. Whether or not this model even approaches the true potential function is not known, since vibrational spectra of the heavier alkaline earth dihalides have not been measured. Measurements of some of the lighter alkaline earth dihalides[50] assigned the frequencies of the bending motion as $BeF_2$ = 825 cm.$^{-1}$, $BeCl_2$ = 482 cm.$^{-1}$, and $MgCl_2$ = 295 cm.$^{-1}$. These frequencies have recently been subject to several criticisms which have been summarized by Hildenbrand.[51] He finds that for the compounds mentioned, these frequencies are much higher than those required to fit experimental entropies. Linevsky, Seshadri, and White[52] have studied the in-

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frared spectrum of $MgF_2$ isolated in inert gas matrices and assigned a strong band near 250 cm.$^{-1}$ to the bending vibration. While we feel that the earlier infrared spectra were carefully examined it is certainly necessary to point out that several studies are in apparent disagreement with our results. It is thus not obvious whether an ionic model is appropriate for the alkaline earth dihalides.

For group IIB dihalides an apparent disagreement sets in immediately if an ionic model is used to fit the geometry. Because the bond lengths in these species are relatively short, nonlinear geometries are predicted, unless extremely low values of the metal ion polarizabilities are used. It is evident that the linearity of $HgF_2$ is surprising from this point of view. Further evidence against the applicability of an ionic model is shown by the halogen quadrupole coupling constants of $CH_3HgCl$ and $CH_3HgBr$. These coupling constants have been measured by Gordy and Sheridan[37] and are only 20% less than in $CH_3Cl$ and $CH_3Br$, respectively. In view of the extremely small value of $(eqQ)_x$ found in the alkali halides and the good correlation between halogen quadrupole coupling constant and chemical bond character, it seems unlikely that an ionic model for the group IIB dihalides is applicable.

It seems, therefore, that at best an ionic model can be used for the group IIA dihalides to give an account of the general trends found. It seems unlikely that the potential function predicted by such a model is correct.

Consider next the structures of the $MX_2$ species in terms of directed valence theory. The ground state of the group II elements is $(ns)^2$ $^1S$, an inert structure, so that it is necessary to consider electron promotion or valence-state preparation. As has been discussed

many times, the linear geometry is readily explained by considering the lowest sp configuration as the valence state. The bent geometry can then be attributed to an sd valence state. Indeed it is found that the energy of the lowest sd configuration with respect to the lowest sp configuration correlates with observed geometry. For those metals for which both geometries are found, it is necessary in addition to assume that sd is favored for short bond lengths. The linearity of $MnF_2$ is then surprising from this point of view since here an sd configuration is quite low lying.[27]

In the absence of detailed and rigorous quantitative calculations it is not at all obvious in what form an explanation of equilibrium geometry should be sought. To our knowledge, it has not yet been proven that the Hartree–Fock function has its minimum energy at the same value of the molecular coordinates as obtains in reality. For diatomic molecules there are arguments, both theoretical and computational, that the difference between the Hartree–Fock and the correct internuclear separation is quite small. In view of the relatively small energy required to bend bonds compared to stretching them it is not obvious, however, that the diatomic molecule can serve as a model for the polyatomic case. Almost all of the present molecular orbital functions for polyatomic molecules are certainly very crude approximations to the Hartree–Fock functions. Thus agreement with observation can be fortuitous or the result of a particular selection of parameters. In view of these uncertainties it is apparent that any simple molecular orbital computation purporting to explain geometries should be viewed with suspicion.

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# A Semiempirical Treatment of Molecular Structures.
# II. Molecular Terms and Application to Diatomic Molecules

BY G. KLOPMAN

A self-consistent semiempirical method which is designed for the calculation of heats of formation and charge distribution of nonconjugated molecules is outlined. The method is based on an antisymmetrized product of molecular orbitals, simplified in such a way as to make the values of all involved integrals directly available from atomic spectra (see paper I[1] of this series where atomic terms have been described and their connection with electronegativity demonstrated) and molecular bond distances. In a preliminary study, this method has been used to calculate satisfactory values of bond energies and reasonable values of charge distributions in 80 diatomic molecules ($\sigma$-bonded).

## I. Introduction

Methods based on linear combinations of atomic orbitals,[2,3] which have proved to be particularly successful in conjugated systems, have been applied mainly in three different ways.

(a) In the case of small or highly symmetrical molecules, the calculations are made as accurately as

possible by using either the Goeppert-Meyer and Sklar approximation[4] or self-consistent field techniques such as the Roothaan[5] method of solving the Hartree–Fock problem for molecules.[6] The approximation common to these methods is giving an analytical form to the atomic orbitals.[7,8]

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