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Aspects of breaking of symmetry through vibrational motions

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Abstract

Varied aspects of breaking of symmetry in crystalline and molecular conditions are considered. Distributions of electronic density about atomic centres of Li and H in crystalline LiH and isolated diatomic molecules of that compound en route to dissociation are discussed in relation to symmetry.

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1. Introduction

Symmetry is a theoretical concept that might be somewhat overrated in chemistry because most molecules lack other than trivial operations of symmetry, as also do most macroscopic samples of chemical matter without deliberate processing towards that end. From a point of view of rigorous quantum mechanics, a molecule in a quantum state has extension in neither space nor time, and therefore has at most spherical symmetry, which is almost devoid of interest. Within a limited range of applicability, symmetry is, however, useful in chemistry not only for both molecular and macroscopic levels but also, with some reservation, for molecular moieties from the point of view of local symmetry.

Symmetry breaking is a term of contemporary technical jargon that seems to have originated among physicists; its meaning is obscure because no actual or

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explicit agent of an action implied in that breaking is evident. Within the apparently acceptable extent of this ill defined term, there exist many chemical examples if one infers some separation or bifurcation to occur because of a diminished symmetry. For instance, tartaric acid separates from aqueous solution into crystals of one or other chiral form. A nominally octahedral complex of a metallic element such as copper might experience a static tetragonal distortion—a compression or elongation-that generates, between a central metallic atomic centre and six adjacent ligands, either two long and four short bonds, or vice versa; an explanation of this effect by Jahn and Teller [1] involves—generally partial—removal of electronic degeneracy through a distortion such that a minimum potential energy of conformation of atomic centres at hypothetical equilibrium occurs at other than the most symmetric conformation according to the total number of feasible operations of symmetry. At a higher temperature, or for other complexes of the same metal, such a distortion might be small enough for the molecular conformation to exhibit a symmetry greater than that expected for a double minimum on a hypersurface of potential energy for the duration of an experimental measurement, according to a dynamic Jahn-Teller effect [2]. As a viable microscopic mechanism of structural transformations in solid substances, a cooperative Jahn-Teller effect was described [3]. Both these static and dynamic effects, and their consequences in regard to accurate determination of structures of molecules and crystals, are likely well known to chemical crystallographers. As a-possibly unique-example of breaking of symmetry for a liquid system, a transition on cooling below the lambda point of helium, specifically ⁴He, about 2.17 K produces, in increasing proportion with further cooling, a superfluid phase that does not separate from the ordinary fluid phase but represents those helium atoms in their state of least energy. Whether analogous cooling of an appropriate molecular liquid substance through a particular temperature might produce multiple distinct mesophases-liquid crystals-is unknown.

As a mechanism active in a dynamic Jahn-Teller effect, an interpretation involves vibrational motion with amplitude large enough to encompass both minima that might occur in a static Jahn-Teller effect. Vibrational motions of this kind produce other effects of interest in spectra or photochemical reactions of small molecular species in the gaseous phase. For instance, although water as H₂O in ice is certainly characterised through experiments with diffraction of x-rays or neutrons as an angular triatomic species, upon absorption of light with energy only about half that of red light—which is still 40 times the thermal energy at 300 K—in the deformation mode, a free molecule vibrates through one minimum of potential energy corresponding to an angle about 1.8 rad through another minimum corresponding to an angle 4.5 rad with the same sense of rotation across a local maximum at π rad; with that energy corresponding to only $v_2 = 5$ for H₂O, the water molecule becomes effectively a linear triatomic species rather than angular [4]. As a linear triatomic molecular species might be envisaged to have greater symmetry than an angular molecule, in this case the vibrational motion of large amplitude in angular deformation involves the enhancing, rather than breaking, of symmetry.

In electronic transitions of free molecules investigated in supersonic jets to simplify spectra, manifestations of Jahn–Teller effects are known for ions benzene with halogen substituents [5] in fluorescence spectra. For molecules containing few atomic centres, molecular spectra in the mid- and near-infrared regions provide information about symmetry breaking of other types. For germane $Ge^{1}H_{4}$, for instance, the rotational fine structure of bands involving extension and contraction of Ge-H bonds alters markedly from that of a spherical rotor in a fundamental vibrational mode, involving alteration of a single vibrational quantum number by only one unit, to that of a merely symmetric rotor, involving one separate Ge-H bond and three other equivalent Ge-H bonds, when quantum numbers associated with stretching modes alter by three units in total [6]. Even in the far infrared region, the pure rotational spectrum of methane ${}^{12}C^{1}H_{4}$ becomes observable in absorption when an axis of a molecule about which free rotation occurs coincides with a CH bond rather than a bisector of such a bond. An approximate model of normal modes has been traditionally applied to interpret vibrational or vibrationrotational spectra associated with the extension or contraction of chemical bonds involving only a single quantum number altering by one unit, for which all atomic centres vibrate in phase with the same frequency, and all equivalent atomic centres have the same amplitude in such a vibrational mode. For a symmetric mode, all equivalent bonds extend or contract in phase, whereas for an antisymmetric or asymmetric mode, some equivalent bonds extend while others contract, all at the same frequency and preserving the relationships of phase, according to a classical description as typically postulated. The wave number of a spectral transition involving such a symmetric mode is almost invariably less than that of an analogous asymmetric or antisymmetric mode, i.e. symmetric $v_1 \sim 365,000 \text{ m}^{-1}$ versus asymmetric $v_3 \sim 375,000 \text{ m}^{-1}$ for ${}^{1}\text{H}_{2}{}^{16}\text{O}$, or symmetric $v_1 \sim 133,300 \text{ m}^{-1}$ versus antisymmetric $v_3 \sim 234,500 \text{ m}^{-1}$ for ${}^{12}\text{C}{}^{16}\text{O}_2$. In contrast, dissociation of these molecules according to such a symmetric motion, such as

$$H_2O \rightarrow 2H + O$$

and

$$CO_2 \rightarrow C + 2O$$

requires much more energy than a partial dissociation, such as

 $H_2O \rightarrow H + OH$

and

 $\mathrm{CO}_2 \to \mathrm{O} + \mathrm{CO}$

that one might associate with an asymmetric or antisymmetric vibrational motion; these partial dissociations are commonly observed in chemical reactions induced by thermal or photochemical means. There must clearly exist some mechanism according to which vibrational energy becomes accumulated in a single bond among those formally equivalent bonds of the same type, to enable a breaking of that bond that implies a concurrent breaking of symmetry. For germane, according to the allusion above, this transition from an approximately *normal mode* for a fundamental band associated with extension and contraction of a bond or bonds to a *local mode* [7] occurs by the second overtone, and similarly for other polyatomic hydrides; vibrational anharmonicity is considered to serve as a mechanism to implement this effect.

For the simplest molecular species ${}^{1}H_{2}^{+}$, described by the symbol X ${}^{2}\Sigma_{g}^{+}$ for its electronic ground state, mere replacement of one atomic nucleus by an isotopic variant, ²H or D, suffices to produce a significant electric dipolar moment, $|\mathbf{p}| \sim$ $1/6 \ eR_e$, or $2.9 \times 10^{-30} \ C \ m$ with $R_e \sim 1.06 \times 10^{-10} \ m$, because the centre of mass of this molecular ion, taken as the origin of coordinates, fails to coincide with the centre of electric charge. Even for a neutral molecular species HD, a small dipolar moment, $|\mathbf{p}| \sim 2.8 \times 10^{-33}$ C m [8], makes feasible an observation of pure rotational and vibration-rotational transitions in absorption in the far, mid and near infrared regions of the electromagnetic spectrum. For the purpose of evaluating radial functions for potential energy and other properties of dihydrogen in its electronic ground state, this effect greatly facilitates experimental detection and characterisation relative to spectral measurements either through Raman scattering at small densities of sample or through absorption induced by intermolecular interactions at large densities, with consequent obscuration of features. In these two cases, and analogously for HCCD etc., an isotopic substitution has the effect of breaking a symmetry that a distribution of electronic density would otherwise impose on the nuclear frame. Even without such isotopic dissymmetry, rotation of methane or silane about an axis through one bond, in contrast to an axis that is a bisector of two bonds, enables observation of pure rotational spectra in absorption, as mentioned above, because such rotation is accompanied by centrifugal distortion that extends three bonds off the axis so as to break the nominal tetrahedral symmetry of the static or equilibrium conformation.

2. LiH from crystal to atoms

Crystalline lithium hydride is not only merely weakly reactive to atmospheric dioxygen and water vapour but also chemically stable against thermal decomposition until at least its melting point at 951 K, unlike other alkali-hydride compounds. Its structure corresponds to that of NaCl, or rather KCl, with six long—and hence weak—bonds, of length about 2.04×10^{-10} m, between a given Li atomic centre and each of its six adjacent H atomic centres, and analogously six weak bonds between H and its six Li nearest neighbours. At a temperature 1223 K, at which vapour above molten Li metal in the presence of gaseous H₂ or D₂ contains LiH or LiD diatomic molecular species, the latter emit infrared light at frequencies corresponding to pure rotational and vibration–rotational transitions [9]. Sublimation of LiH molecules from the surface of crystalline LiH, or the evaporation of LiH molecules from the surface of liquid LiH under the assumption that coordination in a putative liquid phase on average approximates that in a crystal-

line form, hence involves a breaking of symmetry from a cubic environment with centred faces to a diatomic entity of cylindrical symmetry. Whether this crystalline substance is composed essentially of ions or of nearly electrically neutral atoms is uncertain, but for a related compound, Li₂BeF₄, critical analysis of electronic densities seems to indicate a slight preference for almost neutral atomic centres, rather than Li⁺, Be²⁺ and F⁻ ions, present in a unit cell [10]; charges associated with atomic centres are represented as $L_2^{0.18+}$ Be^{0.39+} $F_4^{0.19-}$. The analysis of density of electronic charge in crystalline LiH reported in accessible literature [11] seems to indicate a dense charge near atomic centres of one type, presumably Li, and much more diffuse charge near atomic centres of another type, hence H; such a condition would be consistent with the presence effectively of ions, Li^+ and H^- , in the crystalline lattice, rather than nearly neutral atoms Li and H; a converse situation with diffuse charge about Li and dense charge about H might yield a qualitatively similar pattern. Although the distribution of electronic density about atomic centres of H appears nearly spherical with a slight elongation toward each atomic centre of Li, the effective charges correspond to $Li^{0.96+}H^{0.15-}$ within spherical distributions about atomic centres and 0.81 electrons per formula unit elsewhere.

On the basis of vibration-rotational spectra, LiH is well characterised as a free diatomic molecule in the gaseous phase: the length of a prospective bond between atomic centres Li and H is well defined, in terms of a hypothetical equilibrium internuclear separation $R_e/10^{-10}$ m = 1.59491156 ± 0.00000024; this value includes uncertainties in fundamental constants h and N_A . The permanent electric dipolar moment, hence applicable as the value of a radial function at that equilibrium distance, is $|\mathbf{p}| \sim 19.6 \times 10^{-30}$ C m, or three quarters of what one might expect from the presence of two unpolarised ions with electric charge of unit magnitude at the same distance. According to calculated values of electric dipolar moment \mathbf{p} , which agree closely with experiment in regions in which direct comparison is practicable, the magnitude of **p** increases almost linearly with internuclear distance over a large range about $R_{\rm e}$, before attaining a maximum magnitude near 2.8×10^{-10} m, after which the magnitude of **p** decreases rapidly, eventually proportional to R^{-7} as R becomes large. With extension of the interatomic bond of a molecule of LiH on tending to proceed toward dissociation, this behaviour of **p** indicates an approach towards an ionic limit corresponding to ions Li⁺ and H⁻; in a region about some point R_x , charge transfers from H⁻ to Li⁺ to effect neutralisation such that upon further increase of internuclear distance the molecule moves towards a limit corresponding to neutral atoms Li and H in their electronic ground states. For all known net electrically neutral diatomic molecules in their electronic ground states, dissociation into neutral atoms requires less energy than into ions, consistent with the fact that the energy associated with the affinity of atoms of one type for an electron is less than the energy of ionisation of atoms of the other type. In terms of hypothetical curves for potential energy, as a first approximation one considers such curves for two electronic states X and A of LiH, both of the same class of symmetry, with term symbol ${}^{1}\Sigma^{+}$; although such a curve, or points that might define such a curve, might be readily generated from application of a calculation of molecular electronic structure in which an artificial distinction between electronic and nuclear motions is imposed, no proof of uniqueness of inversion of experimental data to such a curve exists. In ground state X, a molecule near equilibrium separation has, relative to its nuclear frame, a large electric dipolar moment, approaching a magnitude corresponding to ions with unit charge at the same distance, whereas in excited state A, a molecule of LiH has the opposite polarity, Li^-H^+ , of magnitude $\sim 10.2 \times 10^{-30}$ C m, near its large equilibrium distance $\sim 2.6 \times 10^{-10}$ m, but decreasing and eventually reversing its polarity to Li^+H^- at large internuclear distance [12]; binding in these states might be considered to be of roughly ionic and more covalent types, respectively, with some polarisation, whatever else those terms might crudely imply. In accordance with a rule that curves for potential energy of such states of the same class of symmetry do not cross, so to prevent a more strongly bound polar molecule in an approximately *ionic* state from proceeding to an ionic limit across a curve pertaining to a weakly bound *covalent* state that would correlate with a limit of neutral atoms involving diabatic functions for potential energy, the character of these curves alters gradually within a short region of internuclear distance containing an avoided crossing at R_{x} . At this point, curves of potential energy of both interacting states X and A have the same slope or first derivative with respect to internuclear distance, but concavities or second derivatives of opposite signs. As either diabatic or nonadiabatic states at all separations retain the same class of symmetry, there is no breaking of spatial symmetry in such a process. If one considers the intrinsic angular momentum of products, in contrast, a breaking of symmetry does occur: although molecules in both molecular states, and both ions, lack net spin, both neutral atoms resulting from dissociation have doublet states, specifically expressed in a term symbols ²S. The combination of spins for separate atoms might retain singlet character, although individual atoms must be considered to possess doublet character because spectral transitions of electron-paramagnetic resonance become observable for both separate atomic species. Although the Jahn–Teller effect is associated with electronic degeneracy related to net orbital angular momentum, no analogous spatial distortion of crystalline structure is known for net spin angular momentum. Further avoided crossings apply to the curve for the potential energy of LiH in state A, which dissociates not to ions but to atoms, an excited atom Li²P but H²S in its ground state.

Does there exist some property of a diatomic molecule in its electronic ground state that faithfully reflects this transition from strongly polar or nearly ionic to covalent and weakly polar character? The radial function for electric dipolar moment of LiH fails to fulfill this condition because the maximum magnitude occurs at an internuclear separation, 2.75×10^{-10} m, much less than that of the avoided crossing R_x , supposed to occur about 3.857×10^{-10} m [13]. What is required is a property that is sensitive to properties of electronically excited states of the same symmetry class: the vibrational g factor directly satisfies this criterion. Delineated first in a paper by Herman and Asgharian [14] in relation to an effective Hamiltonian for nuclear motion of diatomic molecular species, this vibrational g factor pertains to kinetic energy of motion along the line connecting atomic centres in the same way that the rotational g factor [15] is associated with kinetic energy

of motion perpendicular to that internuclear vector, or rotational motion. The Zeeman effect implies splitting of spectral lines through partial removal of degeneracy due to J, hence showing effects due to distinct values of M_{I} ; for a gaseous sample of a diatomic molecular compound at small density subjected to a magnetic field of appropriate strength and orientation, this splitting, when manifest in the first pure rotational transition, directly affords an expectation value of a radial function for the rotational g factor. This experiment makes practicable the evaluation of a single contribution to the effective Hamiltonian in a way that is impracticable for any other single term. In contrast, no magnetic effect of low order, or other known experiment, yields direct experimental information about the vibrational g factor, but through indirect evidence from experiment—by analysis of vibration-rotational spectra measured in the absence of applied electric or magnetic field with added information—or calculation—about the rotational g factor, one can deduce the existence and properties of that vibrational g factor [16]. Limited by the extent of spectral data, such information from experiment pertains necessarily to only a small region about the equilibrium internuclear separation R_{e} , but no such limitation affects calculation of molecular electronic structure. For the latter purpose, an algorithm has been devised by Bak et al. [17], and the results of calculation by Sauer of the vibrational g factor of ⁷Li¹H [18] appear in a plot in Fig. 1. An extremum evidently occurs near 3.65×10^{-10} m, near a suggested value of this avoided crossing.

The vibrational g factor is hence fascinating because, even though it is formally a property of a particular electronic state—the electronic ground state in cases of interest, it reflects properties of other electronic states, through its relation to non-



Fig. 1. Vibrational g factor, g_{ν} , of ⁷Li¹H as a function of internuclear distance R.

adiabatic vibrational effects involving matrix elements to electronically excited states; for this purpose, the energy denominator implies that the most important interactions with another state having symmetry of the same type involve the energetically nearest electronically excited state. In the case of LiH, such an interaction between states X and A, both of symmetry ${}^{1}\Sigma^{+}$, clearly explains the curious feature of a pronounced minimum in the displayed plot of data for the vibrational g factor; the rotational g factor exhibits no such extremum between its limiting values for the united atom and separate atoms.

3. Conclusion

Despite its formal lack of significant applicability for large and complicated molecules, symmetry has important consequences for small molecules; the breaking of symmetry through vibrational motions produces notable phenomena in relation to molecular structure conducive to crystallographic and spectral observations.

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