On Abnormal Rotation of Molecules

O. OLDENBERG, *Physical Research Laboratory, Harvard University*
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Hypothetical statements, explaining the abnormal rotation of molecules observed in band spectra, are tested by the investigation of the OH bands. It is known that the OH radicals are excited in the electric discharge through water vapor by simultaneous dissociation of H_2O and excitation of OH. As expected, strongly *abnormal* rotation is observed in the *emission* spectrum. On the other hand, the *absorption* spectrum of OH in the electric discharge showing *normal* rotation, confirms the assumption just mentioned regarding the excitation process. By addition of helium the rotation observed in emission is reduced to its normal value; no appreciable persistence of rotation in collisions is evident. In order to judge whether in a given source the temperature can be derived from the *rotational* structure of the band spectrum, tentative rules are deduced from a review of the known processes by which abnormal rotation may be produced or destroyed. The intensity distribution of the *vibrational* structure of a band spectrum indicates the temperature of the gas only in special cases.

I. PROBLEM AND PREVIOUS WORK

THE intensity distribution within a single band of a molecular spectrum, indicating the rotation of the molecules, is ordinarily determined by the temperature. Hence it serves for the measurement of temperatures in stellar atmospheres and electric discharges. In the electric discharge the molecules, emitting the spectrum which is being observed, have just suffered an excitation by electron impact; nevertheless their rotation indicates the temperature because it is not affected to any considerable extent by electron impact. This is understood on the basis of the laws of impact since in the collision between a light and a heavy body no appreciable exchange of kinetic energy takes place. Moreover, it is confirmed by experiments of Harries[1] investigating the kinetics of electrons diffusing through bimolecular gases.

In view of this important method for the determination of temperatures, some striking exceptions are of interest because the intensity distribution in single bands leads to apparent temperatures of several thousand degrees, although the experiments are performed at approximately room temperature. In previous papers[2] two elementary processes have been suggested hypothetically explaining these abnormal "rotational temperatures." An example for one process is the excitation of HgH molecules by impact of the second kind with excited Hg

atoms; experimental proof for this process will be published soon by F. F. Rieke.[3] The other hypothetical process and its experimental confirmation are the objects of the present paper.

It was discovered by Lochte-Holtgreven[4] that the C_2 and CH bands excited in the electric discharge through acetylene (HCCH) gas show abnormal rotation. This has been interpreted by the following hypothesis: The excitation of the HCCH molecule by electron impact leads to a vibration so strong that the excited molecule dissociates into fragments, one of which is excited. This type of process is well known in a diatomic molecule such as I_2, which when dissociated by electron impact or absorption of light, goes over into a pair of atoms one of which might be excited. The energy of *translation* of the atoms so produced is abnormal—that is, independent of the temperature and in most cases much higher than the thermal value—and is determined by a relation between certain potential curves describing the laws of force of the normal and excited molecule. A *polyatomic* molecule in the analogous process ought to produce molecular fragments with abnormal *translation, vibration* and *rotation*. Again, all energies are determined not by thermal equilibrium but instead by a molecular excitation process best described by potential curves. The abnormal *translation* cannot be observed easily. The abnormal *vibration* is not characteristic for this process alone, since the vibration of the

[1] W. Harries, Zeits. f. Physik **42**, 26 (1927).
[2] O. Oldenberg, Phys. Rev. **37**, 194 (1931) and **37**, 1550 (1931).
[3] Cf. F. F. Rieke, Phys. Rev. **42**, 587 (1932).
[4] W. Lochte-Holtgreven, Zeits. f. Physik **67**, 590 (1931).

excited state far exceeds the thermal value anyway in most molecular spectra. The abnormal *rotation* of an excited fragment, for example CH, is to be observed unless it is reduced to the thermal value during the lifetime of the excited state by a large number of collisions. Evidently the simultaneous dissociation of the polyatomic molecule and excitation of one of the fragments are characteristic for this process.

The present paper deals, first, with an experimental proof for this hypothesis derived from the abnormal intensity distribution in the OH bands and, secondly, with the experimental reduction of this rotation to its normal value. In the last section some general rules are tentatively derived.

II. ABNORMAL ROTATION OF OH RADICALS

It has been stated by Bonhoeffer and Pearson[5] that in the electric discharge through water vapor the well-known OH bands at 3064A are excited in one process by simultaneous dissociation of H_2O and excitation of OH. This is concluded from the fact that even for the smallest current, when hardly any OH radicals are present, the intensity of the band is considerable, approximately proportional to the current. The simultaneous dissociation of H_2O and excitation of OH requires an energy of about 9 volts. Obviously it is highly improbable that electron impact should provide just the minimum value of energy required, without any excess, so that the H atom and the OH radical when parting have the kinetic energies of all degrees of freedom within the narrow range of the thermal value of about 1/40 volt. In the normal H_2O molecule the atoms form an angle of 105°, as derived by Mecke and Baumann[6] from the band spectra. The H atom when flying away is producing very probably some rotation of the remaining OH radical. Therefore, our hypothesis leads us to predict abnormal rotation for the well-known OH bands.

Actually, in the spectrum the high rotational energy levels show up with an intensity im-

possible to reconcile with thermal distribution. For example, the line $P_1(29\frac{1}{2})$ comes out with considerable intensity, although from the temperature it is estimated that only one molecule in 10^{23} would have the corresponding rotational energy, evidently much too small a concentration. Thus the observation confirms the prediction that such a process of excitation leads to rotation entirely unrelated to the temperature.

This argument is supported by the absorption spectrum of OH radicals in the electric discharge. Since the fall of 1931 the absorption spectrum of OH has been studied at this laboratory by Dr. M. Grabau and the writer for the investigation of chemical processes. The spectra are to be calibrated with regard to the concentration of OH by an absorption spectrum of OH with known concentration.[7] Recently several failures to observe the absorption spectrum of OH at ordinary temperatures in experiments with electric discharges and chemical reactions have been reported.[8] A possible reason for these failures is that the experiments were undertaken with medium size spectrographs. Actually the most sensitive observation of *faint absorption* lines represents the same problem as the resolution of two *closely adjacent emission* lines. It requires a spectrograph of a resolving power comparable with the width of the absorption lines to be observed. Since the individual lines of the OH bands have a Doppler width of about 0.005A, the second order of a 21-foot grating, having a resolving power of 0.014A, is applicable although a still higher resolving power would be desirable. In this instrument, H_2O vapor with an electric discharge running clearly shows absorption of the strongest band 3064 of OH. The results of these experiments will be reported later.

For the present problem it is of interest that in absorption the single band is short; no trace of the high rotational lines appears. It is to be concluded that the radiating molecules with abnormal rotation do not originate from these OH radicals normally present in the discharge,

[5] K. F. Bonhoeffer and T. G. Pearson, Zeits. f. physik. Chemie **14**, 3 (1931); cf. W. H. Rodebush and M. H. Wahl, J. Chem. Phys. **1**, 606 (1933).

[6] R. Mecke and W. Baumann, Zeits. f. Physik **81**, 463 (1933).

[7] K. F. Bonhoeffer and H. Reichardt, Zeits. f. physik. Chemie **139**, 75 (1928), discovered the thermal dissociation of H_2O into OH and H at temperatures up to 1600°C.

[8] K. F. Bonhoeffer and T. G. Pearson, Zeits. f. physik. Chemie **14**, 1 (1931); P. Harteck, Trans. Faraday Soc. **30**, 139 (1934); W. Frankenburger and H. Klinkhardt, Zeits. f. physik. Chemie **15**, 440 (1932).

but instead from H_2O molecules by simultaneous dissociation and excitation. Evidently, after the radiation process the OH radicals are soon robbed of their abnormal rotation by thermal collisions and only after a somewhat greater interval are consumed in the chemical reaction.

III. The Reduction of the Rotation to its Normal Value

It seemed questionable whether or not the abnormal rotation could be reduced to its normal value by collisions during the lifetime of the excited state. In order to explain the abnormal rotation observed in some fluorescence experiments, alternative hypotheses have been offered, one assuming an extraordinary persistence of rotational energy even through thousands of collisions,[9] the other interpreting the observed spectra simply by the application of classical mechanics to the collision process.[10] These alternatives will be discussed in a paper by F. F. Rieke.

The persistence of rotation of the excited OH radicals is investigated in the following experiment. The rotation of OH is essentially a motion of a light particle, the H atom, circling about the heavier O atom. In order to give it a chance to dissipate its kinetic energy, we must provide for collisions with another light body. during the lifetime of the excited state. Addition of hydrogen might have an undesirable effect, since H_2 molecules may take away the electronic energy as well as the rotation, as is known from several cases of fluorescence radiation; a reduction of *total intensity* would result instead of the reduction of *rotation*.[11] Helium molecules, however, are known not to destroy the electronic

excitation,[12] their mass ought to be sufficiently small to exchange kinetic energy with H atoms.

In Fig. 1 the OH band 3064, photographed with a Hilger E3 quartz spectrograph, is compared (a) in the discharge through water vapor of low pressure with (b) in the discharge through 20 cm helium with a trace of water vapor. The long and complicated band shrinks strikingly into a much shorter and simpler structure. About the origin, two simple branches are to be distinguished easily. The change is not due to a decrease of total intensity as can be seen by comparing the complete disappearance of the edge in the helium experiment with the high intensity of the edge in pure water vapor. Furthermore, the change is not to be described by the quenching of one or the other branch, but instead by the reduction of rotation in every
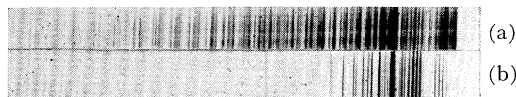

Fig. 1. Effect of admixture of 20 cm He on the intensity distribution of the OH band 3064 in the H_2O discharge. (a) H_2O. (b) H_2O+He.

branch. This was verified by the comparison of spectra taken with a 21-foot grating. (In Fig. 1 the faint branch fading away before it reaches the edge is R_1, the intense branch in the opposite direction, Q_1.) The intensity distribution estimated from the grating spectrum, leads to a temperature of about 670°K.

The comparison of the two spectra demonstrates, first, that in pure water vapor the rotation is highly abnormal and, secondly, that it can be reduced by collisions during the lifetime of the excited state. No particular persistence of rotation in collisions is evident.

An unexpected result is that the complicated band is simplified so strikingly by addition of a rare gas that it might be worth while to try the same method for other complicated bands. Obviously the labor of analyzing the band may eventually be made easier. An exposure taken with the second order of a 21-foot grating revealed the sharpness of the lines unspoiled by the addition even of 20 cm of helium.

[9] H. Beutler and E. Rabinowitsch, Zeits. f. physik. Chemie (B) **8**, 403 (1930).

[10] O. Oldenberg, Phys. Rev. **37**, 194 (1931). It has been pointed out by Franck and Eucken (Zeits. f. physik. Chemie **20**, 460 (1933)) that the transfer of *vibrational* energy in intermolecular collisions as well as in collisions between electrons and molecules, is not to be interpreted by the mechanical picture of dumb-bells colliding with one another. A strong persistence of vibration is assumed in some special cases on the basis of observations of the rates of monomolecular reactions and of dispersion of sound.

[11] The single bands of OH show about the same intensity distribution in water vapor of a few tenths of a mm and 15 mm pressure.

[12] L. v. Hamos, Zeits. f. Physik **74**, 379 (1931).

IV. General Rules for the Determination of the Temperature from Band Spectra

In order to judge whether in a given source the temperature can be derived from the *rotational* or *vibrational* structure of a band spectrum, it is of interest to review the processes determining the intensity distribution observed and in particular the known cases of abnormal distribution.[13]

The following processes are known to lead to abnormal distribution of rotational energy:

(1) Simultaneous dissociation of a *polyatomic* molecule (H_2O) and excitation of one of the fragments (OH) have been discussed in section I.

(2) Excitation of a *diatomic* molecule can under some circumstances result in excess vibration (explained by the Franck-Condon rule), the energy of which is subsequently partly transferred into *rotation* by a few impacts during the lifetime of the excited state. The occurrence of this process has been proved by F. F. Rieke in sensitized fluorescence radiation where the detail can better be followed (HgH bands). The same process must be expected to occur in electric discharges.[14] Experimentally, in the electric discharge through a diatomic gas, only a few cases of abnormal rotation are known, presumably on account of the fact that the accurate determination of the real temperature of the gas is made difficult by the presence of atoms and excited molecules, which show a tendency to deliver their energies to the walls of any thermometer. An example, which possibly might be explained by the principles discussed, has been

discovered by Richardson.[15] The intensity distribution of certain hydrogen bands (in which the intensity is practically confined to the "diagonal bands" 0→0, 1→1, 2→2 and 3→3) changes by the admixture of helium. The high *vibrational* bands are *quenched* but within the 0→0 band the high *rotational* lines are relatively *strengthened*. It might be assumed that in the excitation by electron impact excited hydrogen molecules are produced with *normal rotation* but *high vibration*.[16] In collisions with helium atoms, probably the electronic excitation is not taken away but the excess vibrational energy is distributed over the degrees of freedom available, a part going into translation, another part into rotation of the hydrogen molecule. If only a few collisions take place during the lifetime of the excited state, the rotation might have a chance to pick up a part of the vibrational excess energy before the gradual dissipation of energy is interrupted by the radiation process observed. Thus we understand the appearance of abnormal rotation of the 0→0 band with increasing helium pressure. We expect the abnormal rotation to disappear again at a still higher pressure as described for the OH bands in section III.

(3) The third process to be mentioned, leading to abnormal rotation, is excitation by impact. Smyth and Arnott[17] discovered an abnormally large intensity of the higher rotational states in the N_2 bands when excited by a canal ray. This observation agrees with the theoretical conclusion that the heavy particle of the canal ray, rather than the light electron, is able to transfer energy of rotation to the molecule. The effect observed is not very pronounced. The same effect produced by *fast electrons* giving off a small fraction of their energy into rotation of N_2 molecules, has been observed by Duffendack.[18] It seems certain, however, that the slow electrons

[13] Cf. R. T. Birge, *Molecular Spectra in Gases*, 215–222 (1926); W. Weizel, *Bandenspektren*, 180–184 (1931); W. Jevons, *Band Spectra of Diatomic Molecules*, 133–139 (1932). Undoubtedly more cases are incidentally mentioned in the literature. The following observations of abnormal intensity distribution are left out since the experimental facts are not sufficiently well known: In the band spectrum of helium the band 4650 shows a certain anomaly (W. H. J. Childs, Proc. Roy. Soc. **A118**, 309 (1928)) while the band 6400 fails to show it although both bands belong to similar types of transition (C. W. W. Read, Proc. Roy. Soc. **A134**, 654 (1931)). A unique observation has been reported by N. Thompson (Proc. Phys. Soc. **46**, 440 (1934)), a rotational temperature derived from the N_2+ bands, lower than the temperature of the furnace surrounding the discharge tube.

[14] In the HgH bands, excited in a mixture of Hg and H_2, W. Kapuscinski and J. G. Eymers (Zeits. f. Physik **54**, 246 (1929)) observed an appreciable deviation from the thermal distribution of rotational energy. It is hardly possible, however, to analyze the process involved.

[15] O. W. Richardson, Proc. Roy. Soc. **A111**, 720 (1926) and *Molecular Hydrogen and its Spectrum*, p. 198 (1934); cf. A. S. Roy. Proc. Nat. Acad. Sci. **19**, 443 (1933).

[16] A large change of vibrational quantum number in the excitation process is to be expected from the Franck-Condon rule, since the upper state of the Fulcher bands has a much larger internuclear distance (1.136) than the normal state of the molecule (0.76).

[17] H. D. Smyth and E. G. F. Arnott, Phys. Rev. **36**, 1023 (1930).

[18] Private communication; cf. G. Herzberg, Zeits. f. Physik **49**, 761 (1928).

prevailing in most electric discharges are unable to excite rotation.

(4) An exceptional observation has been made by Gale and Monk[19] and confirmed by Aars.[20] They found the alternation of intensities varying within the individual fluorine bands so that the strong lines and the faint ones would yield different values of the temperature—as far as the observed intensities can be approximated by a thermal distribution. This irregularity is probably caused by a perturbation. A similar effect seems to exist in the CN band 3884.[21]

On the other hand, band spectra in which the rotation of molecules actually indicates the true temperature have been investigated in Ornstein's[22] laboratory. In general, we may expect the rotational structure of a band spectrum to indicate, at least approximately, the true temperature of a gas in the following cases: (1) absorption spectra, characteristic of molecules which have not just been disturbed by an excitation process; (2) emission spectra excited by heat,[23] provided that the intensities are not modified by self-absorption; (3) emission spectra of electric discharges at pressures so low that no collisions take place during the lifetime of the excited state;[24] (4) emission spectra at high pressure, in particular high pressure of added rare gases,

characteristic of molecules which have a good chance to come to thermal equilibrium of rotation during the lifetime of the excited states (OH +He); (5) emission spectra of molecules like N_2 which do not pick up appreciable vibration or rotation—though for different reasons—in the excitation process. It is not claimed that this list is complete.

The rules just mentioned obviously fail to give a definite criterion deciding *a priori* whether or not in an actual spectrum exactly normal rotation is to be expected. It is certain, however, that in many experiments with electric or thermal excitation the rotation actually yields the correct temperature. Only the absorption method is *a priori* certain to indicate the real temperature of the gas by the molecular rotation.

Finally, the determination of the temperature from *vibrational* intensities is to be compared briefly with the method discussed, based on the rotation. In the electric discharge, the rotational intensity serves for this purpose mainly on account of the fact that the *rotational* energy is not appreciably changed in the excitation by slow electrons. The *vibrational* energy, however, is in many cases completely changed, as described by the Franck-Condon rule. Hence the vibrational intensity distribution in the excited state is only indirectly determined by the temperature[25] unless the vibration is brought back to the value of thermal equilibrium by a large number of collisions during the lifetime of the excited state. In many cases it is obviously not even possible to describe the vibrational distribution of the excited electronic level by a virtual temperature. For example, for the halogen molecules excitation by light or electron impact leads predominantly to *high* vibration of the excited level, whereas the thermal distribution of vibration, even for high temperatures, necessarily leads to the maximum population of the *lowest* vibrational level (Maxwell-Boltzmann distribution for one degree of freedom). This explains the failure of Rosseland and Steensholt[26] to derive consistent values of the temperature from

[19] H. G. Gale and G. L. Monk, Astrophys. J. **69**, 77 (1929).

[20] J. Aars, Zeits. f. Physik **79**, 122 (1932).

[21] M. Fassbender, Zeits. f. Physik **30**, 90 (1924).

[22] Examples are cited in a review by L. S. Ornstein, Phys. Zeits. **32**, 517 (1931).

[23] R. T. Birge, reference 13; L. S. Ornstein, H. Brinkman and A. Beunes, Zeits. f. Physik **77**, 72 (1932); D. T. J. Ter Horst and G. Krygsman, Physica **1**, 114 (1933).

[24] Even for no collisions and strict validity of the Franck-Condon rule a minor deviation of the rotational temperature from the thermal value is to be expected if a considerable change of internuclear distance takes place at the excitation process. For example, iodine molecules in the very moment of excitation by electron impact do not appreciably change their rotational energy or internuclear distance because of the small mass of the impinging electron. The excited molecule has a larger equilibrium value of the moment of inertia. Hence the energy quanta of rotation are smaller. The conservation of angular momentum leads to a conservation of *rotational quantum number*, hence to a reduction of *rotational energy*. The excess energy goes into the vibration. (This exchange of energy is easily understood on the basis of potential curves, Zeits. f. Physik **56**, 563 (1929).) Therefore, if no collisions take place during the lifetime of the excited state, the rotation of the excited molecules is expected to correspond to a lower temperature than the rotation of the normal molecules. The ratio of these temperatures is to be estimated from the ratio of the moments of inertia. (Cf. W. R. van Wijk, Zeits. f. Physik **75**, 584 (1932).)

[25] Cf. G. Herzberg, Zeits. f. Physik **49**, 761 (1928). For recent references cf. N. R. Tawde, Proc. Phys. Soc. **46**, 324 (1934).

[26] S. Rosseland and G. Steensholt, Univ. Observ. Oslo Publ. No. 7, p. 14.

the vibrational intensity distribution of the nitrogen bands observed in the aurora.[27] The conclusion is that the chances are not good for determining the temperature of a gas from the vibrational intensities observed in an *electric discharge*. This objection obviously does not hold against the emission spectrum excited by heat[28]

[27] The pressure of these layers of the atmosphere is so low that no collisions during the lifetime of the excited state are to be expected. Handbuch der Experimentalphysik **25**, Part 1, p. 435 (1928).

[28] L. S. Ornstein, H. Brinkmann and A. Beunes, Zeits. f. Physik **77**, 76 (1932).

or the absorption spectrum.[29]

The main conclusion is that hypothetical statements made previously for the interpretation of abnormal rotational intensity distribution in bands are confirmed by the investigation of the OH bands, and general rules are tentatively derived for the determination of the temperature from the rotational and vibrational intensity distribution in band spectra.

[29] Cf. H. Kuhn, Zeits. f. Physik **39**, 77 (1926); E. Hutchisson, Phys. Rev. **36**, 416 (1930); K. Wurm, Zeits. f. Astrophys. **5**, 260 (1932).

The Thermal Resistivity and the Wiedemann-Franz Ratio of Single Crystal Zinc

C. A. Cinnamon, *Physical Laboratory, State University of Iowa*

The thermal resistivities at 57°C are measured for thirteen large, strain-free, single crystals of zinc. The guard tube method is used with the heat applied at the center of the specimen. The results show definitely that the thermal resistivity obeys the Voigt-Thomson symmetry relation. The principal resistivities are $\omega_0 = 0.991$ and $\omega_{90} = 0.936$ cm deg. C/watt, with the ratio $\omega_0/\omega_{90} = 1.058^8$. The close agreement of this value with the ratio of the principal electrical resistivities previously determined in this laboratory shows that the W–F ratio is the same for all orientations of the zinc crystal. The value of this ratio is 7.15×10^{-6} watt ohm/deg. C at 57°C and agrees within 11 percent with the value predicted by the Sommerfeld theory. The two principal thermal conductivities are $\lambda_0 = 1.009^2$ and $\lambda_{90} = 1.068^4$ watts/cm deg. C at 57°C. Some observations are included on "optically mosaic" crystals and on the effects of permanent strain on the single and mosaic crystals.

INTRODUCTION

ALTHOUGH the thermal conductivities of some few zinc crystals of various orientations[1] have been previously measured,[2] only Bridgman has made a definite attempt to check the Voigt-Thomson symmetry relation for thermal conductivity. His results are, unfortunately, so scattered as to render the test inconclusive. From these data Bridgman further concluded that the Wiedemann-Franz ratio is not the same for all orientations of the zinc crystal. Goens and Grüneisen[2(a), (b)], however, find at 20°C nearly the same values for the two principal orientations ($\theta = 0°$ and $\theta = 90°$). The present work consists of an experimental determination of the thermal resistivities of a group of zinc crystals having orientations distributed throughout the possible range, undertaken for the express purpose of studying the variation of thermal resistivity with orientation and of testing the Wiedemann-Franz law.

For the zinc crystal the Voigt-Thomson symmetry relation takes the form

$$\lambda_\theta = \lambda_{90} + (\lambda_0 - \lambda_{90}) \cos^2 \theta, \tag{1}$$

in which λ_θ is the thermal conductivity for orientation θ while λ_0 and λ_{90} are for orientations 0° and 90°, respectively. An exactly similar equation may be written for each of the three quantities: thermal resistivity, ω_θ; electrical conductivity, σ_θ; and electrical resistivity, ρ_θ.[3] Also, for the two principal orientations (0° and 90°) the following reciprocal relations hold:

$$\lambda_0 = 1/\omega_0, \qquad \lambda_{90} = 1/\omega_{90},$$
$$\sigma_0 = 1/\rho_0 \quad \text{and} \quad \sigma_{90} = 1/\rho_{90}. \tag{2}$$

[1] The orientation is the angle, θ, between the normal to the (basal) cleavage plane and the length of the rod.

[2] (a) Grüneisen and Goens, Zeits. f. Instrumentenkunde **46**, 104 (1926); (b) Goens and Grüneisen, Ann. d. Physik **14**, 164 (1932); (c) P. W. Bridgman, Proc. Am. Acad. Arts Sc. **61**, 101 (1926); (d) C. C. Bidwell and E. J. Lewis, Phys. Rev. **33**, 249 (1929).
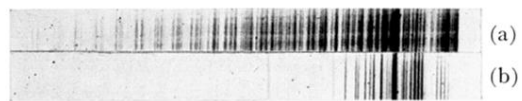
[3] W. Voigt, Lehrbuch der Kristallphysik, Ch. VI.

Fig. 1. Effect of admixture of 20 cm He on the intensity distribution of the OH band 3064 in the H_2O discharge. (a) H_2O. (b) H_2O+He.