Decomposition of Metastable Diatomic Doubly Charged Positive Ions

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Abstract: Energy released upon the dissociation of some doubly charged diatomic molecules into singly charged atoms has been studied with a mass spectrometer. For N_2^{2+}, O_2^{2+}, $NO\cdot^{2+}$, CO^{2+}, I_2^{2+}, Br_2^{2+}, and Cl_2^{2+} close agreement may be established between experimental results and previously calculated theoretical potential energy diagrams. Experimental results are also given for IBr^{2+} and ICl^{2+}.

Among the interesting aspects of the study of metastable molecular ions is the determination of the energy released upon their decompositions. In the case of diatomic molecules, data obtained from the calculation of the energy released in the decomposition of doubly charged ions produced in a mass spectrometer can lead to information concerning the electronic structure of these systems.

The experiments reported in this paper were carried out using an Hitachi Perkin-Elmer RMH-2 double-focusing mass spectrometer.[1] A schematic diagram of this instrument is given in Figure 1. Ions were produced using bombarding electrons having an energy of 80 eV and a sample pressure of approximately 1×10^{-5} torr. The energy spread in the ion beam leaving the electric sector of the mass spectrometer may be measured with a multiplier detector located behind the β slit (the energy-resolving slit). An energy spectrum of the ion beam is produced in the plane of the β slit. If the β slit is sufficiently narrow and the beam is scanned across this slit by varying progressively either the accelerating voltage or the electric sector voltage, an energy profile of the beam is obtained. Measurements have shown[1] that at 5000 V accelerating voltage, the width of the main ion beam is 0.53 V at half-height, 1.20 V at 1% height, and 2.67 V at 0.1% height. The main beam of ions contains all the singly and multiply charged ions which leave the ionization chamber and reach the plane of the β slit without decomposition.

When a singly charged ion of mass m_1 leaves the ionization chamber and falls through the full accelerating voltage V, it acquires a kinetic energy eV. If it then decomposes in the field-free region in front of the electric sector into a singly charged ion of mass m_2 and a neutral fragment of mass m_3, the kinetic energy will be shared among the fragments in proportion to their masses if there is no kinetic energy released at fragmentation. When the detector at the β slit is raised out of the ion beam and the electric sector voltage is reduced to a value $(m_2/m_1)E$ (where E is the value at which the main beam of ions is transmitted) the product ion m_2 will be transmitted through the β slit and can be mass analyzed.[2,3] Alternatively, the electric sector voltage can be kept at the value E but the accelerating voltage increased to a value $(m_1/m_2)V$.[4,5] The product ions of mass m_2 will again be transmitted through the β slit and mass analysis can be performed. Scanning of either the electric sector voltage or the accelerating voltage can thus be used to study these product ions.

The decomposition of doubly charged ions may also be studied in this manner. In this case, the ion m_1^{2+} acquires an energy 2eV in falling through the accelerating field. If an ion of sufficient internal excitation breaks into two singly charged ions of masses m_2 and m_3, they will carry, respectively, mean kinetic energies of $2(m_2/m_1)eV$ and $2(m_3/m_1)eV$. Again, these fragments can be studied by scanning either the electric sector voltage or the accelerating voltage. But in this case there is necessarily a release of kinetic energy in the decomposition due to the separation of the positive charges and this will result in broadening of the observed peaks. Indeed, broadening of these "metastable peaks" due to the fragment ions arises entirely from energy release and the widths of the metastable peaks can be used to calculate this energy.[6] The formulas and calculations relating the energy release, T, and width of the metastable peak for the decomposition of doubly charged ions into two singly charged ions have been given.[7] They show

$$T = (eV/32)(m_1^2/m_2m_3)(\Delta E/E)^2 \qquad (1)$$

and

$$T = (eV/4)(m_2^2/m_1m_3)(\Delta V/V)^2 \qquad (2)$$

In these equations, E and V are the normal electric sector and accelerating voltages, and ΔE and ΔV are the widths of the metastable peaks when scanning the electric sector or the accelerating volts, respectively. The values E_1 and V_1 which represent the adjusted values of sector voltage or accelerating voltage corresponding to the center of the peak due to m_2 product ions are given by

$$E_1 = 2E(m_2/m_1) \qquad (3)$$

and

$$V_1 = (V/2)(m_1/m_2) \qquad (4)$$

Knowing m_1, these equations can be used to calculate m_2. Equations 1 and 2 show that for a particular value of energy release, the observed fractional width $\Delta E/E$ or

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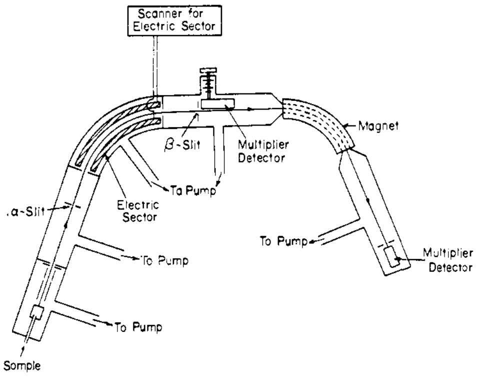

Figure 1. Schematic diagram of Hitachi Perkin-Elmer RMH-2 double-focusing mass spectrometer.

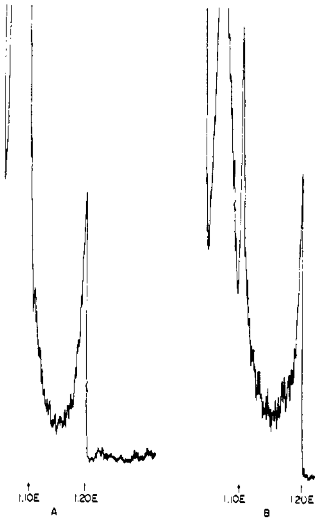

Figure 2. Partial ion kinetic energy spectrum for CO^{2+} showing dish-topped peak for the transition $CO^{2+} \rightarrow C\cdot^{+} + O\cdot^{+}$ (A) at 3.8 kV, (B) at 6.0 kV.

$\Delta V/V$ will vary as $V^{-1/2}$. Thus, in order to obtain the best resolution, V should be as high as possible.

When there is a release of kinetic energy in a decomposition, the edges of the observed peak will correspond to those decompositions in which the product ion has been accelerated or decelerated along its original direction of motion. For a decomposition in which the product ion receives a component of velocity perpendicular to this direction, the product ion may not pass through the final collector slit, and this discrimination effect will result in distortion of the shape of the observed peak from a Gaussian form to a more "rounded" peak, or in extreme cases to a peak with a "dished" top.

If it is assumed that the energy released in the decomposition of a doubly charged ion is due solely to simple Coulombic repulsion between two point charges, then the distance, r, between the two charge centers in the original ion at the point of decomposition can be estimated from the relationship $T = e^2/r$. In this equation, e is the electronic charge and r is the intercharge distance. For a diatomic molecule, this calculation gives an upper limit to this distance, for, even on this simple assumption, part of the total energy of the decomposing molecule may be due to covalent effects.

In this work the decomposition of a number of doubly charged diatomic molecules was studied in terms of the energy released. A more detailed interpretation of the results is attempted for the ions N_2^{2+}, O_2^{2+}, and $NO\cdot^{2+}$ in terms of the potential energy diagrams. For the other diatomic molecules only a brief discussion of the results is given. The detailed experimental conditions will be described for the case of carbon monoxide. Extra experimental difficulties associated with the study of symmetrical molecules such as N_2 and with the study of molecules containing heavy isotopes at high natural abundance such as ICl and IBr will be discussed separately. The results obtained are listed in terms of the measured kinetic energy release and the calculated "intercharge distance."

Results

When CO^{2+} decomposes to give the ions $C\cdot^{+}$ and $O\cdot^{+}$, two dish-topped peaks are observed when the electric sector voltage is scanned[1] centered at values $1.14E$ and $0.86E$, respectively (see eq 3). At an accelerating voltage of approximately 3.8 kV, the low-energy edge of the dish-topped peak at $1.14E$ overlaps with an "artifact" peak in the energy spectrum (see Figure 2A). The high-energy edge of the dish-topped peak occurs at $1.20E$. The artifact peak, seen in all energy spectra obtained on the RMH-2 mass spectrometer, is believed to be due to reflection of ions and neutral particles when the deflected main ion beam strikes the walls of the electric sector. The overlapping of these two peaks makes it extremely difficult to measure the width of the dish-topped peak. However, this difficulty may be circumvented in several ways. The first involves increasing the accelerating voltage to give better energy resolution. Figure 2B shows a scan of the same region of the energy spectrum of CO as shown in Figure 2A, but at an accelerating voltage of approximately 6.0 kV. Both edges of the dish-topped peak are now clearly seen at approximately $1.0E$ and $1.2E$, allowing measurements of the peak width to be made.

A second method of circumventing the problem of overlapping energy peaks involves raising the multiplier detector at the β slit, setting the magnet to transmit the daughter ion of the transition, and then scanning the accelerating voltage at a fixed electric sector voltage. The ions are detected at the final collector. This type of scan is referred to as an HV scan. Thus, for the charge separation transition in CO^{2+}, HV scans were obtained corresponding to transmission of the ions $O\cdot^{+}$ and $C\cdot^{+}$ at both mass 16 and mass 12. It can be seen from Figure 3 that, in the case of mass 16, a large dish-topped peak appears centered at 87.6% HV, with edges at approximately 83.2 and 91.8% HV. In addition to this peak, there is another dish-topped peak closer to the main ion beam, centered at about 95.2% HV, with edges at approximately 92.5 and 98.0% HV. This peak is a "lens" peak, *i.e.*, a peak due to the identical transition as the one at 87.6% HV, but due to decompositions in the lens system of the RMH-2 mass spectrometer.[1] This lens has a field-free region within it in which metastable transitions may occur. These lens peaks, however, are easily identified because their position on the energy scale varies with the potential of the lens system, while those peaks due to transitions in the first field region do not.

For the charge-separation transition for CO^{2+}, the energy released has been calculated from both the energy spectrum obtained by scanning the electric sector

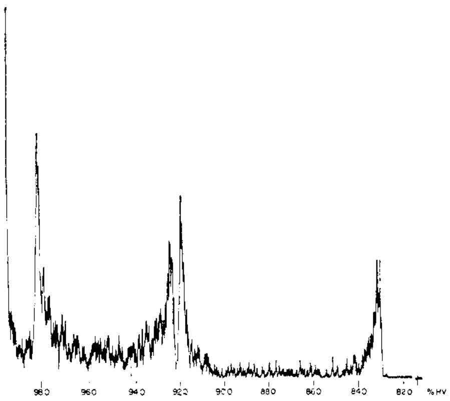

Figure 3. HV scan of CO^{2+} at *m/e* 16.

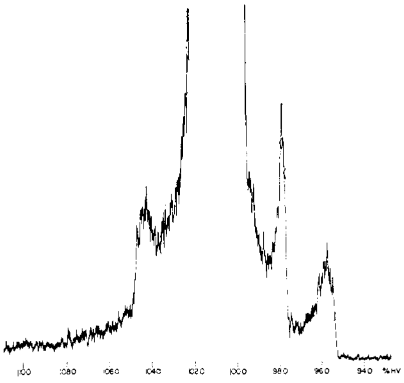

Figure 4. HV scan of $I_2{}^{2+}$ at *m/e* 127.

and from the accelerating voltage scans. From the peak at 1.14E (due to mass 16) in the energy spectrum, T was calculated to be 5.50 eV. This calculation was made from the data obtained at 6.0 kV (Figure 2B). The energy released in such a decomposition is independent of the accelerating voltage; the values of T calculated for this transition at other accelerating voltages did not vary from the mean by more than approximately 2.5%. The peak at 0.86E in the energy spectrum (due to mass 12) could not be sufficiently separated from an artifact peak to permit a measurement. From the accelerating voltage scans, the width of the peak at mass 16 (Figure 3) gave a value of 5.59 eV for T, while that at mass 12 gave 5.67 eV. These results, listed in Table I, are in good agreement with each other and also with those obtained from the measurements on the energy spectra. From the mean of 5.59 eV released in the decomposition, an equivalent "intercharge distance" was calculated to be 2.57 Å.

Table I. Energy Released (T) and Equivalent Charge Separation (r) in Transitions of Doubly Charged Diatomic Molecules

Transition	Type of measurement	T, eV	r, Å
$CO^{2+} \rightarrow C\cdot^{+} + O\cdot^{+}$	Energy scan	5.52	2.61
	HV scan, *m/e* 16	5.59	2.57
	HV scan, *m/e* 12	5.67	2.54
$N_2{}^{2+} \rightarrow N^{+} + N^{+}$	HV scan, *m/e* 14	6.22	2.31
$O_2{}^{2+} \rightarrow O\cdot^{+} + O\cdot^{+}$	HV scan, *m/e* 16	8.03	1.79
$NO\cdot^{2+} \rightarrow N^{+} + O\cdot^{+}$	HV scan, *m/e* 16	6.15	2.34
$I_2{}^{2+} \rightarrow I^{+} + I^{+}$	HV scan, *m/e* 127	3.96	3.63
${}^{79}Br_2{}^{2+} \rightarrow {}^{79}Br^{+} + {}^{79}Br^{+}$	HV scan, *m/e* 79	4.25	3.39
$({}^{79}Br^{81}Br)^{2+} \rightarrow {}^{79}Br^{+} + {}^{81}Br^{+}$	HV scan, *m/e* 79	4.36	3.30
	HV scan, *m/e* 81	4.18	3.44
${}^{35}Cl_2{}^{2+} \rightarrow {}^{35}Cl^{+} + {}^{35}Cl^{+}$	HV scan, *m/e* 35	4.79	3.00
$({}^{35}Cl^{37}Cl)^{2+} \rightarrow {}^{35}Cl^{+} + {}^{37}Cl^{+}$	HV scan, *m/e* 35	4.55	3.16
$({}^{127}I^{79}Br)^{2+} \rightarrow {}^{127}I^{+} + {}^{79}Br^{+}$	HV scan, *m/e* 127	3.00	4.80
$({}^{127}I^{35}Cl)^{2+} \rightarrow {}^{127}I^{+} + {}^{35}Cl^{+}$	HV scan, *m/e* 127	3.82	3.77

When symmetrical diatomic molecules (*e.g.*, O_2, N_2, I_2, etc.) are studied in this manner, the problem of overlapping energy peaks becomes more acute. Since the daughter ion of a charge-separation decomposition retains exactly half the energy of the original ion, it appears in the energy spectrum at exactly the same position as the peak due to the main ion beam. Although the main ion beam is very narrow (about 0.5 V wide at half-height), it is approximately 10^5 times larger in intensity than the metastable peak, resulting in this peak being lost in the wide skirts of the main ion beam. Therefore, energy spectra cannot be used at present to measure the energy released in the fragmentation of symmetrical doubly charged ions. If an HV scan is obtained, the same problem exists—but to a much lesser degree. In this case, only one mass of the main ion beam is collected and its intensity is closer to that of the peak due to the metastable transition. Therefore, in the skirts of the main ion beam, the edges of the peak due to the transition can be seen. This is illustrated for I_2 in Figure 4 which shows an HV scan at mass 127. The large narrow peak at 100% HV is due to the stable ions of mass 127. At approximately 95.6% HV and 104.8% HV, the edges of the dish-topped peak can be seen due to the reaction

$$I_2{}^{2+} \longrightarrow I^{+} + I^{+}$$

Again, the edge of a lens peak can be seen in Figure 4 close to the main ion beam at 97.8% HV. However, this does not present a problem since it is easily identified. From these spectra, the widths of the peaks can be measured and the energy released in the decomposition calculated. The results of these experiments are given in Table I.

Heavy isotopic ions can present a problem in some cases. Consider the charge separation decomposition of ICl^{2+}. Although an unsymmetrical diatomic ion of this type gives rise to observable peaks in both the energy spectrum and HV scan spectrum, overlapping pairs of peaks are obtained with both methods due to the presence of isotopes. For ICl^{2+}, the following transitions occur

$$ {}^{127}I^{35}Cl^{2+} \longrightarrow {}^{127}I^{+} + {}^{35}Cl^{+} \qquad \text{(I)}$$

$$ {}^{127}I^{37}Cl^{2+} \longrightarrow {}^{127}I^{+} + {}^{37}Cl^{+} \qquad \text{(II)}$$

Since the relative abundances of the two chlorine isotopes are approximately in the ratio 3:1, overlapping peaks whose abundances are in this ratio will be seen for these transitions. Figure 5 shows these peaks in the energy spectrum due to ${}^{127}I^{+}$ formed from molecular ions of mass 162 and 164. Similarly, when an HV scan is carried out at mass 127, two overlapping peaks are seen. The voltages at which they are centered are given by eq 4 as $\{(127 + 35)/[2(127)]\}V = 63.78$ V and $\{(127 + 37)/[2(127)]\}V = 64.57$ V, respectively. However, the ions of masses 35 and 37 can each only arise from a single ionic species and thus will give rise to single peaks. In the case of a molecule like Br_2, $ClBr$, Cl_2, etc., all masses in the HV scans show isotope peaks.

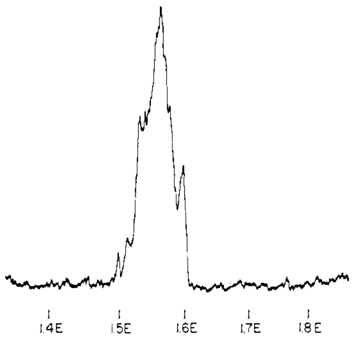

Figure 5. Partial ion kinetic energy spectrum for ICl^{2+} showing dish-topped peaks for the transition $ICl^{2+} \rightarrow I^+ + Cl^+$.

Although these spectra, consisting of isotope and lens peaks, are quite complicated, measurements of peak widths can be made. The high-energy edge of the dish-topped peak due to the heavier isotope will always be seen, as will the low-energy edge of the peak due to the lighter isotope. Since the centers of these peaks can be predicted their widths can thus also be calculated. The results of measurements on compounds of this type are also given in Table I.

Interpretation of N_2^{2+}, O_2^{2+}, and $NO\cdot^{2+}$ Results

Spectroscopic data pertinent to the study of doubly charged molecules are relatively scarce. For the N_2^{2+}, O_2^{2+}, and $NO\cdot^{2+}$ systems, however, sufficient internuclear distances and spectroscopic ionization potentials are known, so that details of the decomposition of these molecules may be investigated. In particular, Hurley[8] has made theoretical estimates of the $E(R)$ curves for a number of the lower electronic states of these systems, which bear directly upon the decomposition process.

In Figure 6 are sketched typical $E(R)$ curves for a hypothetical nonrotating charged and uncharged diatomic molecule AB.[9] Only one state for each charged species is indicated. At larger distances the total energy of A^+ and B^+ varies as e^2/R, while the total energy of A^{2+} and B remains more nearly constant. At some intermediate distance, however, these two total energies approach each other and will cross, except in the case that the electronic states of $(A^{2+} + B)$ and of $(A^+ + B^+)$ have the same spin and space symmetry. Then crossing does not occur, and the situation depicted in Figure 6 is observed.

The net process caused by electron bombardment in the ionization chamber of the mass spectrometer

$$AB + e^- \longrightarrow AB^{2+} + 3e^- \qquad (5)$$

is assumed at some stage to produce the AB^{2+} species either in any of its metastable rotation-vibrational levels below the maximum in the effective AB^{2+} potential curve (horizontal lines in Figure 6) or in the repulsion region above that maximum (diagonally shaded region in Figure 6), such that dissociation into A^+ and B^+ proceeds directly. If the ionization process, (5), occurs in one step "vertically," there will be a distribution over all states of AB^{2+}, as given by the appropriate Franck–Condon factors, having a maximum at the energy level indicated by the head of the left-most arrow in Figure 6.[10] Alternative multistep processes, however, will lead to different distributions.

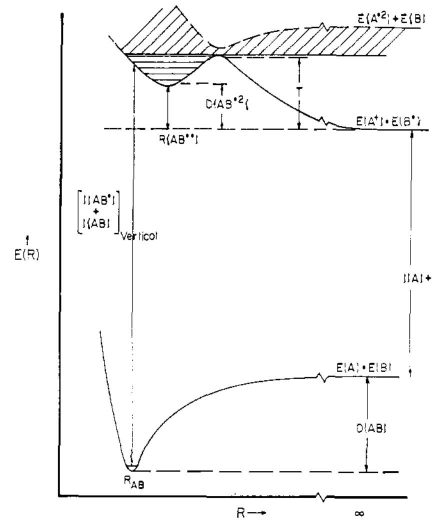

Figure 6. Potential energy curves, $E(R)$, for hypothetical AB and AB^{2+}. Note: the left-most vertical arrow represents the assumed most probable excitation. The upper dashed curve is the companion to the upper solid curve, both of which result from the interaction of states of the same symmetry arising from $(A^+ + B^+)$ and $(A^{2+} + B)$.

In the metastable case, the lifetime of any state will be long compared to the time required for the measurement process ($\sim 10^{-5}$ sec), except for vibration-rotation states lying within a few tenths of an electron volt from the top of the hump.[8] In this last event, outward tunneling may occur. The resulting A^+ and B^+ ions thus produced proceed toward their accessible ground electronic states at infinite separation, ultimately liberating the relative kinetic energy, T.

The $E(R)$ curves for several electronic states each of N_2^{2+}, O_2^{2+}, and $NO\cdot^{2+}$ constructed by Hurley are reproduced in Figure 7. From them and from the data he gives, one can directly compare the calculated differences in energy between the relative maxima and the dissociation products. In each case, one must note that more highly excited electronic states of each doubly charged molecular ion may be formed first by the excitation process. Allowed electronic transitions, however, should occur well within the 10^{-5}-sec limit, bringing these molecules to lower electronic states of the same spin multiplicity.[11] Thus, only the radiationally stable electronic states presumably need be considered here.

Specifically, in N_2^{2+}, the $d^1\Sigma_u^+$, $c^1\Pi_g$, and $A^3\Pi_g$ states should pass quickly to the $a^1\Sigma_g^+$, $b^1\Pi_u$, ${}^3\Sigma_g^-$, and $X^3\Pi_u$ states, though conserving spin. In $NO\cdot^{2+}$, the $B^2\Sigma^+$ should pass to either the $A^2\Pi$ or the $X^2\Sigma^+$ states. In O_2^{2+}, the $C^3\Pi_u$ state should pass to $B^3\Pi_g$ and both should go on to $A^3\Sigma_u^+$, which dissociates into two $O^+(^4S)$ ions. The $a^1\Pi_g$, $a^1\Sigma_u^-$, and $w^1\Delta_u$ states may undergo transitions among themselves, but all dissociate into two $O^+(^2D)$ ions. The $B^3\Sigma_u^-$ and $B^3\Pi_g$ states should both terminate in the metastable $A^3\Sigma_u^+$ state.

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[8] A. C. Hurley, *J. Mol. Spectrosc.*, 9, 18 (1962).

[9] For the simple molecule He_2^{2+}, for example, see L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," McGraw-Hill, New York, N. Y., 1935, pp 347–348.

[10] G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, Van Nostrand, New York, N. Y., 1950, pp 194 ff, 391 ff.

[11] Reference 10, p 24. "Forbidden" transitions may also occur, of course, which would facilitate populating the lower electronic states, though at slower rates.

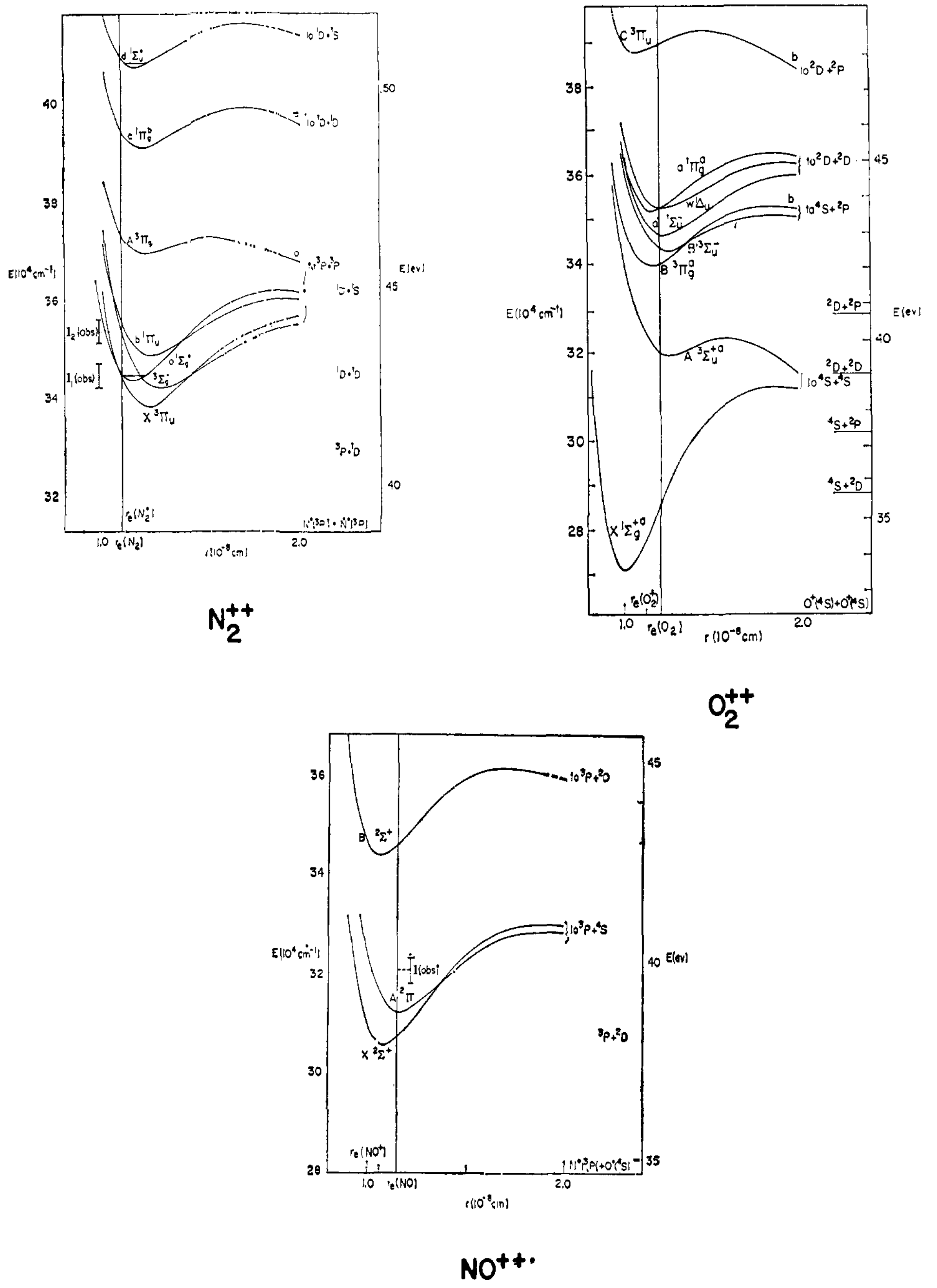

Figure 7. Potential energy curves for N_2^{2+}, O_2^{2+}, and $NO\cdot^{2+}$. This figure is taken from ref 8 with the permission of *J. Mol. Spectrosc.* The copyright is held by Academic Press.

For N_2, Hurley's calculations indicate a considerable vibrational activation of the N_2^{2+} species formed in any of the four states $X^3\Pi_u$, $^3\Sigma_g^-$, $a^1\Sigma_g^+$, and $b^1\Pi_u$, all of which dissociate into two $N^+(^3P)$ ions. Neglecting rotational contributions, the calculated maxima in these states lie at 5.7, 5.4, 6.2, and 6.3 eV, respectively, above the energy of the separated ions. Our experimental data suggest only a single major process, with $T = 6.22$ eV, very close to the predictions derived from the singlet states.

Assuming the validity of our interpretation of the metastable dissociation process, one concludes either (a) that Hurley's calculations are quite accurate and mainly the lowest two singlet states of N_2^{2+} are formed and measured or (b) that, if triplet states are formed in the initial excitation process, Hurley's calculated curves are too low in the region of the hump by about 0.5 eV.

For O_2^{2+}, the internuclear distance in its $X^1\Sigma_g^+$ ground state is calculated to be 0.2 Å shorter than in O_2;[8] even so, a vertical excitation from O_2 intercepts the $X^1\Sigma_g^+$ $E(R)$ curve well below its maximum, so that relatively less vibrational excitation near the top of its hump should be produced directly. The other probably significant metastable states ($w^1\Delta_u$, $a^1\Sigma_u^-$, and $A^3\Sigma_u^+$) have longer internuclear distances, though the $E(R)$ curves are more shallow in the region of metastability, which may lead to significant vibrational excitation, particularly in $A^3\Sigma_u^+$.

For O_2^{2+} molecules produced in the upper vibrational levels of $w^1\Delta_u$ and $a^1\Sigma_u^-$, Hurley's calculations predict that tunneling would yield two $O^+(^2D)$ ions at $T = 5.9$ and 5.6 eV, respectively; likewise, those tunneling from $X^1\Sigma_g^+$ and going to two $O^+(^4S)$ ions are expected in that same range of kinetic energy, at $T = 6.5$

eV. These T values are about 1.5 to 2 eV less than the observed $T = 8.03$ eV. On the other hand, $\mathrm{A}^3\Sigma_u^+$ is estimated to yield two $\mathrm{O}^+(^4\mathrm{S})$ ions at $T = 7.8$ eV, which is only 0.2 eV less than the observed value.

The recorded spectrum shows no evidence of processes occurring at other than 8.03 eV and is in substantial agreement with theoretical prediction, if the predominant metastable species decomposes from the $\mathrm{A}^3\Sigma_u^+$ state. Otherwise, one would conclude that Hurley's $E(R)$ curves are estimated too low by about 2 eV. In this event a clear-cut identification of a metastable state would likely be impossible.

Finally, in $\mathrm{NO}\cdot{}^{2+}$, the predicted T values of 6.4 and 6.3 eV resulting from $\mathrm{X}^2\Sigma^+$ and $\mathrm{A}^2\Pi$, respectively, producing $\mathrm{N}^+(^2\mathrm{P}) + \mathrm{O}^+(^4\mathrm{S})$ are only slightly removed from the observed $T = 6.15$ eV.

Hurley was able only to consider doublet states of $\mathrm{NO}\cdot{}^{2+}$, and so no consideration of possible quartet states can be made here.

It may be noted with the N_2 and O_2 systems that closest agreement with predictions was obtained in our assumed process when the predominant species is a dissociable metastable doubly charged ion assigned to a high vibrational level of the same electronic spin state as the parent neutral diatomic.

Internuclear distances corresponding to maxima in the $E(R)$ curves believed to be significant here may be estimated from Figure 7. They are approximately 1.9, 1.6, and 1.9 Å for N_2^{2+}, O_2^{2+}, and $\mathrm{NO}\cdot{}^{2+}$, respectively, compared to the upper limits given in Table I as 2.31, 1.79, and 2.34 Å, respectively. Thus can be clearly seen the extent of covalency effects (*e.g.*, interaction with states arising from $\mathrm{A}^{2+} + \mathrm{B}$) in lowering the purely Coulombic repulsion between the A^+ and B^+ ions at distances approaching normal bond lengths.

Similar agreement between theory and experiment is found among the other cases listed in Table I. In the course of earlier work, Hurley and Maslen[12] calculated theoretical T values for CO^{2+}, Cl_2^{2+}, Br_2^{2+}, and I_2^{2+} of 56.8, 4.70, 4.28, and 3.7 eV, respectively.[13] These results also stand in excellent agreement with corresponding experimental values presented in Table I. Interpretations of the other experimental data should yield to a similar treatment when the appropriate theoretical $E(R)$ calculations become available.

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[12] A. C. Hurley and V. W. Maslen, *J. Chem. Phys.*, **34**, 1919 (1961).

[13] A. C. Hurley, personal communication.

Solubility of Water in Compressed Carbon Dioxide, Nitrous Oxide, and Ethane. Evidence for Hydration of Carbon Dioxide and Nitrous Oxide in the Gas Phase[1]

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Abstract: The solubility of water in compressed carbon dioxide, nitrous oxide, and ethane has been measured over pressure ranges of 1-60 atm and temperatures ranging from 25 to 100°. Second cross virial coefficients representing deviations from ideality caused by gas-water pair interactions have been evaluated from these data. The cross virial coefficients involving water with carbon dioxide and nitrous oxide are found to be considerably more negative than those for water with ethane at all temperatures. The anomalously large values of these coefficients for water with carbon dioxide and nitrous oxide are interpreted as indicating that a reversible hydration reaction occurs between these gases and water vapor in the gas phase. Values of K_{eq} and the standard enthalpies and entropies of reaction for these equilibria are estimated.

Hildebrand and Scott[2] have presented considerable evidence based on solubility data for the existence of specific chemical interactions involving carbon dioxide, nitrous oxide, and acetylene with many solvents in the liquid phase. In the CO_2–water system, an acid–base reaction is postulated, resulting in the formation of carbonic acid. Considerably less is known regarding the association of nitrous oxide or acetylene with such solvents. There is some evidence that these gases behave in a similar manner in the gas phase. Prausnitz and coworkers[3a] have examined PVT properties of the ammonia–acetylene system and conclude that weakly bound complexes exist in gaseous mixtures of these two compounds. Other evidence[3b] indicates that CO_2 forms a very weak complex with naphthalene vapor at room temperature while N_2O does not.

This paper reports measurements of the solubility of water in compressed carbon dioxide, nitrous oxide, and ethane which were carried out in order to assess the nature and significance of any chemical forces that

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[2] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold, New York, N.Y., 1950; reprinted by Dover Publications, New York, N. Y., 1964, p 248.

[3] (a) H. Y. Cheh, J. P. O'Connell, and J. M. Prausnitz, *Can. J. Chem.*, **44**, 429 (1966); (b) A. D. King, Jr., *J. Chem. Phys.*, **49**, 4083 (1968).