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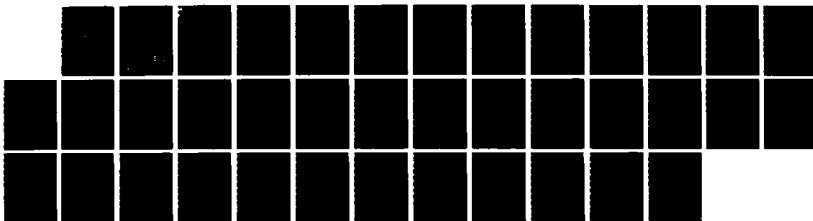
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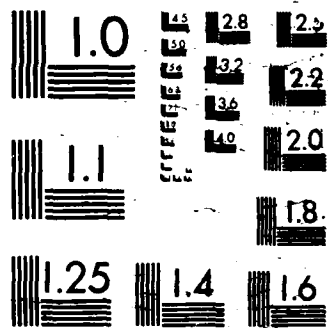
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Interaction of Xe^+ and Cl^- Ions and Their Formed Molecules with a
Xe Solid Matrix

by

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Prepared for Publication

in

Journal of Chemical Physics

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Interaction of Xe^+ and Cl^- Ions and Their Formed
Molecules with a Xe Solid Matrix

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Abstract

Xenon (+) Chloride (-) $\text{Xe}_2^+(\text{Cl})^-$

The aim of the present work is the calculation of the energy of ionic xenon-chlorine systems which can be formed in solid Xe by irradiation. The energy levels of these ionic systems differ from those in the gas phase due to polarization and dispersion interactions with solid Xe atoms. It is shown that the Xe_2^+Cl^- molecule is responsible for experimentally-observed emission. The activation energy of the Xe_2^+Cl^- formation is found to form a broad band.



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I. Introduction

Excited ionic rare gas-halogen molecules are of great interest, particularly because of their lasing properties. These molecules have been well investigated in the gas phase, both experimentally and theoretically.¹⁻⁶ Recent experiments performed by Fajardo and Apkarian⁷ have demonstrated that ionic xenon-chlorine molecules can also be formed in a Xe solid matrix. The spectral transitions in these molecules in the solid phase are not the same as in the gas phase due to interactions between the ionic molecules and the surrounding solid atoms. Such interactions are considered in the present paper in order to study the electronic transitions in the ionic xenon-chlorine molecules inside the Xe solid matrix.

The paper begins with the experimental background in Section II, both gas phase and solid phase, and then proceeds with the theoretical analysis of the molecule-matrix interaction in Section III. The numerical analysis of the Xe_2^+Cl^- molecule and the activation complex for ionic state formation is presented in Sections IV and V, and Section VI is the Conclusion.

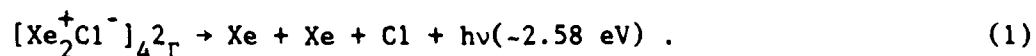
II. Experimental Background

A. Xe^+Cl^- and Xe_2^+Cl^- Molecules in the Gas Phase

The formation of excited molecules $(\text{XeCl})^*$ and $(\text{Xe}_2\text{Cl})^*$ by laser irradiation has been observed in Xe/Cl_2 gas mixtures.¹⁻³ These molecules are ionic in nature and hence are denoted by Xe^+Cl^- and Xe_2^+Cl^- .⁴⁻⁶ The Xe^+Cl^- molecule is formed as a result of the absorption of two separate ultraviolet photons. The first of these photons hits a Cl_2 molecule and produces by photodissociation the Cl atoms. The second photon at $h\nu = 4.02$ eV provided specifically by an XeCl excimer laser is absorbed by a colliding $\text{Xe} + \text{Cl}$ pair transferring an electron from Xe to Cl and forming the excited Xe^+Cl^- molecule.² The electronic structure of the XeCl system is shown in

Fig. 1.² The two lowest states, X and A, are formed by neutral Xe and Cl(²P) atoms. The ground state is weakly bound by 0.035 eV and becomes repulsive at relatively short interatomic distances, $R \leq 3.1 \text{ \AA}$.⁸ The two excited ionic states are similar: both have a deep minimum and form excited ionic molecules due to the attractive electrostatic forces. The photon excites the system to the B state, but due to the crossing of potential curves, the molecule can go to the excited C state from which a radiative transition to the repulsive A state becomes possible with the emission of a photon of 3.54 eV ($\lambda = 350 \text{ nm}$).

The emission of the 350 nm photons is partly quenched by the formation of the triatomic ionic molecules Xe_2^+Cl^- due to the three-body collisions of the Xe^+Cl^- molecule with two Xe atoms.⁶ The Xe_2^+Cl^- molecule is stabilized relative to the Xe^+Cl^- molecule by a strong $\text{Xe}^+\text{-Xe}$ valence attraction. Due to the lower energy of the excited $4^2\Gamma$ state, radiative emission from Xe_2^+Cl^- is red-shifted compared to the Xe^+Cl^- emission. The Xe_2^+Cl^- emission is observed as a wide band with its center at $\lambda = 480 \text{ nm}$ (2.58 eV),



Energy levels of the Xe_2Cl system have been calculated by the diatomics-in-molecules method,^{9,10} and the potential curves are shown in Fig. 2. The equilibrium point of the lower ionic state ($4^2\Gamma$) was obtained for the interatomic distances $R_{\text{Xe-Cl}} = 3.32 \text{ \AA}$ and $R_{\text{Xe-Xe}} = 3.29 \text{ \AA}$, where the three atoms form a triangle with almost equal sides. The calculated Xe-Cl interatomic distance is larger than the interatomic distance in the diatomic Xe^+Cl^- molecule, where the latter has been experimentally measured as $2.94 \text{ \AA}$ and calculated as $3.22 \text{ \AA}$.⁴ However, the Xe-Xe distance in the Xe_2^+Cl^- molecule is close to the interatomic distance of the Xe_2^+ molecule, $3.27 \text{ \AA}$.¹¹ The Xe_2^+Cl^- molecules demonstrate lasing at $\lambda = 518 \text{ nm}$, which is

shifted some 30 nm from the center of the usual Xe_2^+Cl^- emission at $\lambda = 480$ nm.⁵

B. Formation of Ionic Xenon-Chlorine Emission Centers in Xe Solid

The formation and emission of the ionic xenon-chlorine centers has been observed in Xe solid by Fajardo and Apkarian.⁷ The experiments were performed with Xe solid containing Cl_2 molecules as an impurity in the proportion 1/100-1/5000. After the solid was irradiated by 308 nm laser light, the emission was detected at $\lambda = 570$ nm. This emission can be interpreted, as in the gas phase, by the photodissociation of Cl_2 followed by the formation of the excited ionic Xe-Cl system due to the absorption of the next photon. According to the experiment,⁷ only one excited ionic center (most probably Xe_2^+Cl^-) is formed since only one emission band ($\lambda = 570$ nm) is observed in the solid, contrary to the gas mixture where two ionic molecules (Xe^+Cl^- and Xe_2^+Cl^-) can be formed with two different emission wavelengths. The Xe^+Cl^- molecules, if they are formed in the solid, are expected to relax quickly to the more stable Xe_2^+Cl^- molecule. The experiments have also been performed with Xe solid containing HCl molecules, and these demonstrate the same spectroscopic properties as in the case of $\text{Cl}_2 + \text{Xe}$ solid system. The conclusion can thus be made that after the photodissociation of either Cl_2 or HCl, the atoms of these molecules are completely separated in the solid without any influence on one another. Simultaneously with the optical emission, the $\text{Cl}_2 + \text{Xe}$ and $\text{HCl} + \text{Xe}$ solid systems demonstrate electrical conductivity, implying that the formation of the excited ionic centers is accompanied by the excitation of current carriers.¹²

We shall consider in the present work below the following problems:

(1) the calculation of the wavelength shift in the Xe_2^+Cl^- emission in the

solid compared to the gas-phase emission; and (2) the consideration of the activation complex and the calculation of the excitation energy for the Cl + Xe solid system transition to the ionic state. We shall not take into account the vibrational motion of the solid atoms.

III. Molecule-Rare Gas Solid Matrix Interaction

By a molecule in a rare gas solid matrix, we understand a system of atoms (ions) with much stronger inner interactions than the interactions between the molecule and the matrix atoms. This definition is obvious for the case of neutral atoms or strongly bonded molecules, like Cl₂ or HCl doped in rare gas solid. However, for the case where the molecule includes rare gas atoms of the host lattice (Xe⁺Cl⁻ molecule, for example), the definition of the molecule may be ambiguous.

Considering molecules inside a rare gas matrix we shall make three important assumptions: (i) the electronic bands of the rare gas solid are so narrow that the solid structure does not change the interatomic potential curves from those in the gas phase;¹³ (ii) the valence (exchange) interactions between the atoms of the molecule and the matrix atoms can be neglected; and (iii) the coupling between the neutral and ionic states of the molecule can be neglected, and therefore the neutral and ionic molecules (Xe₂Cl and Xe₂⁺Cl⁻, for example) can be considered independently. The first of these assumptions is well defined, so we shall discuss the two other assumptions only.

The valence interaction between a molecule and matrix can be important in the case of ionic molecules R_n⁺ and R_n⁺X⁻ (X and R are halogen and rare gas atoms, respectively) where the positive charge is partly delocalized between the molecular rare gas atoms R⁺ and the matrix atoms. This valence interaction has been discussed in the literature for the case of R₂⁺ molecule

in an R matrix,¹³⁻¹⁵ and in Ref. 13 the neglect of the valence interaction was proposed. The error resulting from the neglect of the molecule-matrix valence interaction for Xe_n^+Cl^- molecule in Xe matrix will be estimated in Section V.

The coupling between the neutral and ionic states of the trapped molecule is weak due to the high energy of the rare gas atoms excitation and small overlap of orbitals. The weakness of the coupling in the Xe-halogen atom interaction is well demonstrated by the results of an ab initio calculation.⁴ This calculation examines the charge transfer between the Xe and halogen atoms which can be considered as a measure of the coupling. The charge transfer decreases with the interatomic distance, and for the Xe-Cl system, for example, it becomes smaller than 10% when the Xe-Cl distance exceeds 3 Å. In the Xe matrix the distance between trapped atoms and Xe atoms is usually larger than 3 Å, and consequently the coupling is small. The weakness of the coupling is supported also by an experimental study of the spectrum of homonuclear halogens trapped in a rare gas matrix. The interaction $U_{AM}^{(s)}$ between these molecules and the solid matrix is mainly of van der Waals origin, and therefore it is small and does not differ significantly for different electronic states. It follows that in the absence of coupling the molecular electronic states are expected to be practically the same as in the gas phase, in accord with the experiment.¹⁶

The above assumptions greatly simplify the consideration of the system, since the total energy of the molecule (A) and the matrix (M) can be expressed as a sum of the molecular energy ($E_A^{(g)}$), the solid matrix energy ($E_M^{(s)}$) and the energy of the molecule-matrix interaction ($U_{AM}^{(s)}$),

$$E_A^{(s)} = E_A^{(g)} + E_M^{(s)} + U_{AM}^{(s)}. \quad (2)$$

The molecular energy $E_A^{(g)}$ is the same as in the gas phase for the corresponding geometry, which can be different than the equilibrium gas phase geometry. The matrix energy $E_M^{(s)}$ is the energy of interaction between matrix atoms excluding those of them which belong to the molecule. In Eq. (2) and below the values associated with the gas phase and solid state are distinguished by the upper indexes (g) and (s), respectively.

For the case of a neutral molecule which does not have a dipole moment, the term $U_{AM}^{(s)}$ in Eq. (2) is equal to the sum of diatomic interaction potentials between the molecule and the matrix atoms. For the case of a molecule which generates an electric field, in particular an ionic molecule, the polarization of the matrix atoms has to be taken into account. The polarization energy can not be presented as a sum of diatomic interactions, so it is calculated separately whereas the polarization terms are excluded from the diatomic potentials:

$$E_A^{(s)} = E_A^{(g)} + E_M^{(s)} + \sum_i \sum_j \bar{U}_{ij} + \epsilon_p. \quad (3)$$

Here ϵ_p is the polarization energy, i and j are atomic indices of the molecule and the matrix, respectively, and $\bar{U}_{ij}$ are the interatomic interactions without polarization terms,

$$\bar{U}_{ij} = U_{ij} - (-A_p/R_{ij}^4), \quad (4)$$

where U_{ij} is the diatomic potential, R_{ij} is the interatomic distance, and $-A_p/R_{ij}^4$ is the polarization term which is valid for ion-atom and ion-ion interactions only. When both atoms are neutral, $\bar{U}_{ij}$ coincides with U_{ij} .

The energy ϵ_p of the solid matrix polarization can be calculated by forming around the ionic molecule an Onsager cavity and considering the solid matrix outside the cavity as a continuum,¹⁷

$$\epsilon_p = \epsilon_{p,c} + \epsilon_{p,o} \quad (5)$$

where $\epsilon_{p,c}$ is the polarization energy of the atoms inside the cavity and $\epsilon_{p,o}$ is the polarization energy of the continuum outside the cavity. The dipole moments of the polarized atoms are assumed to be formed by charged atoms. The polarization energy of the atoms inside the cavity includes also the dipole-dipole interaction

$$\epsilon_{p,c} = -A_p \sum_{j=1}^J \sum_m Z_{j,m}^2 + 2\alpha A_p \sum_i \sum_{j(>i)} \sum_m \sum_n \gamma_{ij,mn} Z_{i,m} Z_{j,n}, \quad (6)$$

where $m = 1, 2, 3$ denote the x, y, z projections of the $\vec{Z}_j$ vectors which are proportional to the field. When the field is formed by a diatomic ionic molecule, then $J = 2$ and

$$\vec{Z}_j = - \frac{\vec{R}_j - \vec{R}_0}{R_{0j}^3} + \frac{\vec{R}_j - \vec{R}_1}{R_{1j}^3}. \quad (7)$$

When the field is formed by a triatomic ionic molecule, like Xe_2^+Cl^- , then $J=3$ and

$$\vec{Z}_j = - \frac{\vec{R}_j - \vec{R}_0}{R_{0j}^3} + \frac{\vec{R}_j - \vec{R}_1}{2R_{1j}^3} + \frac{\vec{R}_j - \vec{R}_2}{2R_{2j}^3}. \quad (7')$$

The matrix of the dipole-dipole interaction is

$$\gamma_{ij,mn} = 3(\vec{R}_j - \vec{R}_i)_m (\vec{R}_j - \vec{R}_i)_n / R_{ij}^5 - \delta_{mn} / R_{ij}^3, \quad (8)$$

where δ_{mn} is the Kronecker delta. In the expressions (6)-(8) i and j are the indices of the matrix atoms, $\vec{R}_0$ is the position vector of the negative ion, and $\vec{R}_1$ and $\vec{R}_2$ are the position vectors of the positive rare gas ions. The parameter A_p is proportional to the rare gas atom polarizability α ,

$$A_p = \alpha e^2 / 2. \quad (9)$$

The contribution of the dipole-dipole interaction to the polarization energy (6) depends on the atoms localization and the dielectric constant.¹⁸ In the present calculation the contribution of the dipole-dipole interaction stands for 25-30 % of the total polarization energy. The polarization of the continuum outside the cavity is considered in the dipole approximation,¹⁷

$$\epsilon_{p,o} = - \frac{\epsilon - 1}{2\epsilon + 1} \frac{e^2 \rho^2}{r_0^3}, \quad (10)$$

where ϵ is the dielectric constant of the solid, ρ is the distance between opposite charges within the ionic molecule, and r_0 is the radius of the cavity.

The atom-atom potentials are expressed in this paper either by the Lennard-Jones expression

$$U(R) = \epsilon_0 [(R_0/R)^{12} - (R_0/R)^6] \quad (11)$$

or by representing the repulsive term by an exponential function,

$$U(R) = A_r \exp(-aR) - A_d / R^6, \quad (12)$$

where A_d is the dispersion coefficient. The ion-atom potential includes

also the polarization term

$$U(R) = A_r \exp(-aR) - A_d/R^6 - A_p/R^4. \quad (12')$$

The polarization coefficient is determined by Eq. (9). The energies of the electronic states are denoted below by E , the interatomic potentials by U , the energies of system formation by V , and the transition energies by T .

IV. Xe_2^+Cl^- Molecule in a Xe Solid Matrix

The crystal structure of the Xe solid is face-centered cubic (fcc) with four atoms per unit cell. Each atom in the lattice is surrounded by 12 nearest neighbors with the distance $\ell = a/\sqrt{2}$ and 6 next neighbors with the distance a , where a is the lattice constant.¹⁹ The Xe lattice constant is $a = 6.197 \text{ \AA}$ for $T = 58 \text{ K}$, and correspondingly the minimal interatomic distance is $\ell = 4.38 \text{ \AA}$.²⁰ The minimal distance ℓ extrapolated to 0 K is only 0.7% smaller ($4.35 \text{ \AA}$).²¹ All further calculations are performed with $\ell = 4.38 \text{ \AA}$.

The radius of a negative ion Cl^- is $1.82 \text{ \AA}$,²² -83% of the Xe atom radius ($2.19 \text{ \AA}$), so it is possible to assume that Cl^- replaces one Xe atom without deforming much the surrounding lattice. Because of the small difference between the radii of Cl^- and Xe, the Cl^- ion can be shifted inside the lattice cage by small distances only. We thus assume that Cl^- is located at a lattice point, whereas the relaxation of the Xe atoms is admitted. The formation of the Xe_2^+Cl^- molecules has to be considered now as a shift of two neighboring Xe atoms with a common charge of $+1$ towards the Cl^- ion.

The interaction energy between the atoms inside the Xe_2^+Cl^- molecule is much larger than the interaction energy between the Xe_2^+Cl^- molecule and the Xe matrix, so it is reasonable to assume that the geometry of the Xe_2^+Cl^-

molecule in the solid matrix is the same as in the gas phase. Computational results support this assumption since the interatomic distances of the Xe_2^+Cl^- molecule in solid are found to be larger than those in the gas phase by 0.1 Å only. As the Xe_2^+Cl^- molecule has the form of a triangle with almost equal sides where the angles are close to 60°, the two Xe atoms which form the Xe_2^+Cl^- molecule are shifted in the lattice along crystallographic lines. The coordinates of some of the atoms are presented in Table 1. The Cl^- ion is located at the origin of the coordinate system ($\vec{R}_0 = 0$).

A. Energy of the $\text{Xe}_2^+\text{Cl}^- \rightarrow \text{Xe}_2\text{Cl}$ Transition

The energy of the transition (1) in the Xe solid is

$$T_{\text{Xe}_2^+\text{Cl}^-}^{(s)} = E_{\text{Xe}_2^+\text{Cl}^-}^{(s)} - E_{\text{Xe}_2\text{Cl}}^{(s)} . \quad (13)$$

Here $E_{\text{Xe}_2^+\text{Cl}^-}^{(s)}$ is the Xe_2^+Cl^- energy in solid, and $E_{\text{Xe}_2\text{Cl}}^{(s)}$ is the energy of two neutral Xe atoms and one Cl atom in the solid with the interatomic distances equal, according to the Franck-Condon approximation, to the corresponding distances in the Xe_2^+Cl^- molecule. The interatomic interactions $\bar{U}_{ij}$ in Eq. (3) can be restricted to the nearest-neighbor pairs. For the Xe_2^+Cl^- case they include the interactions of the Cl^- ion with 10 Xe atoms located around the ion and the interaction of each of two $\text{Xe}^{1/2+}$ atoms with 10 nearest matrix atoms,

$$E_{\text{Xe}_2^+\text{Cl}^-}^{(s)} = E_{\text{Xe}_2^+\text{Cl}^-}^{(g)} + E_M^{(s)} + 10 \bar{U}_{\text{XeCl}^-} + U_{\text{Xe}_2^+\text{M}} + \epsilon_p . \quad (14)$$

$$U_{\text{Xe}_2^+\text{M}} = 2(3\bar{U}_{1,3} + \bar{U}_{1,13} + 4\bar{U}_{1,14} + 2\bar{U}_{1,16}) , \quad (15)$$

where $\bar{U}_{ij}$ stands for the interaction between the $\text{Xe}^{1/2+}$ atom ($i = 1$) and different matrix atoms with different interatomic distances (see Table 1).

The Xe_2Cl energy is

$$E_{\text{Xe}_2\text{Cl}}^{(s)} = E_{\text{Xe}_2\text{Cl}}^{(g)} + E_M^{(s)} + 10U_{\text{XeCl}} + 2U_{\text{XeM}}, \quad (16)$$

$$U_{\text{XeM}} = 3U_{\text{XeXe}}(R_{1,3}) + U_{\text{XeXe}}(R_{1,13}) + 4U_{\text{XeXe}}(R_{1,14}) + 2U_{\text{XeXe}}(R_{1,16}), \quad (17)$$

where $E_{\text{Xe}_2\text{Cl}}^{(g)}$ is the energy of the Xe_2Cl system in the configuration of the Xe_2^+Cl^- molecule, and the R_{1j} are the distances between the $i = 1$ Xe atom and nearest-neighbor matrix atoms (see Table 1). In accord with the Franck-Condon approximation, the matrix energy $E_M^{(s)}$ is the same in Eqs.(14) and (16).

In order to calculate the energy of transition (13) one needs to know the polarization energy ϵ_p and the following diatomic potential curves: U_{XeCl} , $\bar{U}_{\text{XeCl}^-}$, U_{XeXe} , and $\bar{U}_{\text{Xe}^{1/2+}\text{Xe}}$. The polarization energy (5) will be calculated using the radius of the Onsager cavity $r_0 = 7.83 \text{ \AA}$. The cavity with this radius includes centers of all 23 ($i = 3, 4, \dots, 25$) Xe atoms which are the nearest neighbors of the atoms of the Xe_2^+Cl^- molecule, and only one of these is close to the cavity border. Approximately 8 atoms located wholly or partly inside the cavity are not included in the sum (6), since these atoms are not the nearest neighbors of the Xe_2^+Cl^- molecule, and thus their contribution to the polarization energy is small (less than 10%). The dielectric constant of Xe solid is $\epsilon = 2.1$,²⁰ and the distance between opposite charges within the Xe_2^+Cl^- molecule is $\rho = 2.86 \text{ \AA}$. The polarization coefficient (9), which is proportional to the Xe atom polarizability $\alpha = 4.05 \text{ \AA}^3$,²³ is equal to $A_p = 29.14 \text{ eV \AA}^4$. Substituting A_p , ϵ , ρ and r_0 into the expressions (6)-(8), one obtains $\epsilon_{p,c} = -0.34 \text{ eV}$, $\epsilon_{p,o} = -0.05 \text{ eV}$ and $\epsilon_p = -0.39 \text{ eV}$.

The Xe-Cl potential is expressed by Eq. (12) which fits the ground state potential of Ref. 8 for $R > 3 \text{ \AA}$. The coefficients of the Xe-Cl

potential are found to be $a = 2.3 \text{ \AA}^{-1}$, $A_r = 248 \text{ eV}$ and $A_d = 206 \text{ eV \AA}^6$. The experimental potential curve of the Xe-Xe interaction²⁴ is well fitted by the Lennard-Jones potential (11) with the coefficients $\epsilon_0 = 0.096 \text{ eV}$ and $R_0 = 3.98 \text{ \AA}$.

The halogen ion-rare gas atom interaction potential was suggested to be expressed as a sum of a repulsive exponential term and an electrostatic (polarization) term.^{25,26} However, these two terms do not fit well the known halogen ion-rare gas atom potentials, so that the expression (12') with a dispersion term was used to fit the recent experimental Xe-Cl⁻ potential.²⁷ The coefficients of this potential were found to be $a = 3.85 \text{ \AA}^{-1}$, $A_r = 31670 \text{ eV}$ and $A_d = 60 \text{ eV \AA}^6$. The polarization coefficient is $A_p = 29.14 \text{ eV \AA}^4$. The discrepancy between the analytical potential (12') and the experimental values does not exceed 0.005 eV for $R > 3.1 \text{ \AA}$. The potentials for some other halogen ion-rare gas atom pairs²⁸ can be also fitted by the potential (12'). The Xe-Cl⁻ potential $\bar{U}$ which appears in the Eq. (14) is determined by the expression (12), i.e., without the polarization term - A_p/R^4 .

Unfortunately, the Xe^{1/2+}-Xe $\bar{U}$ potential cannot be determined in the same way as in the Xe-Cl⁻ case. The Xe⁺-Xe potential is known,¹¹ but the nature of this potential is complicated and includes valence, electrostatic polarization and dispersion effects which cannot be separated from one another. However, taking into account that the size of the Xe⁺ ion is not supposedly much different from that of the Xe atom, we assume that the repulsive and van der Waals interactions between Xe⁺ and Xe (or Xe^{1/2+} and Xe) atoms is the same as between two neutral Xe atoms. According to its definition [Eq. (4)], the $\bar{U}$ potential of the Xe⁺-Xe interaction does not include the polarization term. It does not include also the valence

attraction due to the neglect of charge delocalization between a molecule and the matrix. It follows that the repulsive and van der Waals terms remain only. Assuming that these terms are equal to the corresponding terms of the Xe-Xe interaction, one obtains

$$\bar{U}_{\text{Xe}^+ \text{Xe}} = \bar{U}_{\text{Xe}^{1/2+} \text{Xe}} = U_{\text{XeXe}}. \quad (18)$$

The equality of the $\text{Xe}^{1/2+}$ -Xe $\bar{U}$ potential to the Xe-Xe potential greatly simplifies the expression (13) for the energy of transition. Substituting in (13) the expressions (14) and (16), we obtain the transition energy expression, which does not include any Xe-Xe interactions,

$$T_{\text{Xe}_2^+ \text{Cl}^-}^{(s)} = T_{\text{Xe}_2^+ \text{Cl}^-}^{(g)} + \epsilon_p + 10[\bar{U}_{\text{XeCl}^-}(\ell) - U_{\text{XeCl}}(\ell)], \quad (19)$$

where $T_{\text{Xe}_2^+ \text{Cl}^-}^{(g)} = 2.56$ eV is the transition energy in the $\text{Xe}_2^+ \text{Cl}^-$ gas molecule² and $\ell = 4.38$ Å is the minimal interatomic distance in the Xe lattice. It is assumed in Eq. (19) that all Xe matrix atoms are located at the lattice points. This assumption is supported by the results of calculations which indicate a small shift of -0.1 Å only for atoms surrounding the $\text{Xe}_2^+ \text{Cl}^-$ molecule. Substituting into the expression (19), the values of the polarization energy ($\epsilon_p = -0.39$ eV) and the potentials ($\bar{U}_{\text{XeCl}^-}(\ell) = -0.006$ eV, $U_{\text{XeCl}}(\ell) = -0.019$ eV), one obtains that the transition energy of $\text{Xe}_2^+ \text{Cl}^-$ in the solid is $T_{\text{Xe}_2^+ \text{Cl}^-} = 2.30$ eV (Fig. 3), and consequently the wavelength is $\lambda = 540$ nm. This value is close to the experimental wavelength of the center of the emission band (570 nm).⁷ The shift in the transition energy within the solid relative to the gas-phase value is -0.26 eV as compared to the experimental value of -0.38 eV.

B. Energy of the Xe_2^+Cl^- Formation

We now calculate the energy of the formation of the excited Xe_2^+Cl^- state from the initial Cl + Xe solid system, with a Cl atom in the center of a cage. The calculation shows that in the initial system the relaxation of 12 Xe atoms of the cage towards the Cl atoms is small, i.e., only 0.06 Å. This relaxation is neglected, and consequently all Xe atoms are located at lattice points. In the initial Cl + Xe solid system we consider separately a neutral Xe_2Cl system with the energy

$$E_{\text{Xe}_2\text{Cl}}^{(s)}(\ell) = E_{\text{Cl}} + 2E_{\text{Xe}} + U_M^{(s)} + 12U_{\text{XeCl}}(\ell) + 21U_{\text{XeXe}}(\ell). \quad (20)$$

The energy of formation is equal to the difference between the Xe_2^+Cl^- energy (14) and the Xe_2Cl energy (20),

$$\begin{aligned} V_{\text{Xe}_2^+\text{Cl}^-}^{(s)} &= E_{\text{Xe}_2^+\text{Cl}^-} - E_{\text{Xe}_2\text{Cl}}(\ell) \\ &= V_{\text{Xe}_2^+\text{Cl}^-}^{(g)} + 10\bar{U}_{\text{XeCl}}(\ell) - 12U_{\text{XeCl}}(\ell) + U_{\text{Xe}_2^+M} - 21U_{\text{XeXe}}(\ell) + \epsilon_p, \end{aligned} \quad (21)$$

where $U_{\text{Xe}_2^+M}$ is determined by expression (15) and

$$V_{\text{Xe}_2^+\text{Cl}^-}^{(g)} = E_{\text{Xe}_2^+\text{Cl}^-}^{(g)} - (E_{\text{Cl}} + 2E_{\text{Xe}}) \quad (22)$$

is the energy of the formation of the Xe_2^+Cl^- gas molecule, equal to 3.62 eV.¹⁰ The potentials in the expression (20) for $\ell = 4.38$ Å are: $U_{\text{XeCl}}^- = -0.006$ eV, $U_{\text{XeCl}} = -0.019$ eV, $U_{\text{Xe}_2^+M} = -0.24$ eV, $U_{\text{XeXe}} = -0.024$ eV.

Inserting these values and ϵ_p in Eq. (21), one obtains $V_{\text{Xe}_2^+\text{Cl}^-}^{(s)} = 3.66$ eV (Fig. 3). This value is close to the Xe_2^+Cl^- energy formation in the gas phase.

The experimental threshold of the Xe_2^+Cl^- formation in the Xe matrix is $\lambda = 370$ nm or $h\nu = 3.35$ eV,⁷ so that our theoretical value is overestimated

by 0.3 eV, at least. It is important to note that the calculation of the formation energy is of lower accuracy compared to that of the transition energy calculation [Eq. (19)], as it involves more potentials.

V. The Activated Xe^+Cl^- and $\text{Xe}_{12}^+\text{Cl}^-$ Complexes for Ionic State Formation

As mentioned above, the Xe_2^+Cl^- molecule is formed in the Xe solid due to the excitation of the system by a photon. The excitation must be considered as the transition of an electron to the Cl atom from one of the adjacent Xe atoms. The ionic system which is formed after the electron transition (but before the atomic relaxation) can be considered as an activated complex. According to the Franck-Condon principle, the atoms of the activated complex are located at the same points as in the initial Cl + Xe solid system. We shall consider two possible structures of this complex. The first is Xe^+Cl^- with the positive charge located on one Xe atom, and the second is $\text{Xe}_{12}^+\text{Cl}^-$ with the positive charge delocalized among all 12 Xe atoms around the Cl^- ion. Which of these two structures is realized as an activation complex depends on the time τ_d of the positive charge delocalization (or the lifetime of the localized structure). If this time is smaller than the period of light oscillations τ_ω , then the $\text{Xe}_{12}^+\text{Cl}^-$ system must be considered as the activated complex, at least for the case where the Cl atom is located in the center of the cage. For the opposite case where $\tau_d \gg \tau_\omega$, the positive charge remains on one Xe atom and the Xe^+Cl^- system plays the role of the activated complex. The lifetime of the localized Xe^+ is on the order of $\tau_d = \hbar/2\pi\epsilon_v$, where ϵ_v is the energy of the valence interaction between the Xe^+ and Xe atoms. For the underformed lattice, the Xe^+ -Xe distance is $\ell = 4.38 \text{ \AA}$ and the valence energy is approximately 0.3 eV,¹¹ which gives $\tau_d \approx 2 \times 10^{-15} \text{ s}$. This time is on the order of visible light oscillations which excite the Cl + Xe solid system. Since it is not

clear which of the two systems is the activated complex, we shall consider both of them.

A. The activated Xe^+Cl^- Complex

The energy of the Xe^+Cl^- activation complex depends on the location of the Cl atom in the cage. The size of the Cl atom is smaller than the minimal Xe-Xe distance, so that the Cl atom can be shifted in the cage toward one of the surrounding Xe atoms. While these Xe atoms can also be shifted toward the Cl atom, it is possible to neglect this shift, as it was shown to be small (Section IV.A). In order to find the position of the Cl atom inside a cage, the potential of the atom was calculated as a function of the shift δ from the center. It was found that this potential changes within the limit of 0.0007 eV only for $\delta \leq 0.8 \text{ \AA}$ and begins to rise significantly after the point $\delta = 0.9 \text{ \AA}$. Similar results were obtained also in Ref. 7, where for the temperature of 12 K the thermal energy is $kT = 0.001 \text{ eV}$, so that the Cl atom can be moving practically free around the cage center within the boundary $\delta < 0.8 \text{ \AA}$. We shall calculate below the Xe^+Cl^- activation energy for both the central Cl position ($\delta = 0$) and the shifted one with $\delta = 0.8 \text{ \AA}$.

The energy of the Xe^+Cl^- system formation in solid phase with Cl at the center ($\delta=0$) is

$$V_{\text{Xe}^+\text{Cl}^-}^{(s)}(\ell) = I_{\text{Xe}} - A_{\text{Cl}} + U_{\text{Xe}^+\text{Cl}^-}^{(g)}(\ell) + 11\bar{U}_{\text{XeCl}^-}(\ell) - 12U_{\text{XeCl}}(\ell) + \epsilon_p, \quad (23)$$

where $I_{\text{Xe}} = 12.13 \text{ eV}$ is the Xe ionization potential, $A_{\text{Cl}} = 3.68 \text{ eV}$ is the Cl electron affinity, and $U_{\text{Xe}^+\text{Cl}^-}^{(g)}$ is the Xe^+Cl^- potential. The polarization energy ϵ_p in (23) can be calculated by using the expressions (5)-(9). It is found to be equal to $\epsilon_p = -0.49 \text{ eV}$. The Xe^+Cl^- potential is equal to

$U_{\text{Xe}^+\text{Cl}^-}(\ell) = -3.37$ eV. Inserting these numbers into Eq. (23) along with the values for $U_{\text{XeCl}}(\ell)$ and $U_{\text{XeCl}}(\ell)$ (see the previous section), we obtain

(s)

$V_{\text{Xe}^+\text{Cl}^-}(\ell) = 4.75$ eV (Fig. 3).

For the case of Cl atom shifted by $0.8 \text{ \AA}$ from the cage center, all interactions are the same as for the $\delta = 0$ case except for the Xe^+Cl^- interaction, which is $U_{\text{Xe}^+\text{Cl}^-} = -4.08$ eV. Consequently, the activation

(s)

energy is $V_{\text{Xe}^+\text{Cl}^-} = 3.94$ eV. Comparing this value with the upper limit obtained for $\delta = 0$, one finds that the Xe^+Cl^- activation energy in the Xe solid matrix forms a band which is in the range $3.94 \text{ eV} \leq V_{\text{Xe}^+\text{Cl}^-} \leq 4.75 \text{ eV}$.

B. The $\text{Xe}_{12}^+\text{Cl}^-$ Complex.

Let us now consider the $\text{Xe}_{12}^+\text{Cl}^-$ system formed by the Cl^- ion located in the center of the cage formed by 12 Xe atoms with the common charge +1. The atomic Xe polarization time is much shorter than the time of delocalization, and therefore the polarization of the lattice follows the motion of the positive charge among the 12 atoms of the $\text{Xe}_{12}^+\text{Cl}^-$ system. Consequently, the polarization energy is determined by the Cl^- ion and one Xe^+ ion and is equal to the polarization energy of the Xe^+Cl^- system. It follows that the $\text{Xe}_{12}^+\text{Cl}^-$ energy differs from that of the Xe^+Cl^- complex by the valence energy of delocalization,

$$V_{\text{Xe}_{12}^+\text{Cl}^-}(\ell) = V_{\text{Xe}^+\text{Cl}^-}(\ell) + \epsilon_v(\ell) . \quad (24)$$

Quantum chemistry considerations show that in the fcc lattice the delocalization energy is

$$\epsilon_v = \sqrt{n}\beta_o, \quad \beta_o < 0 , \quad (25)$$

where n is the number of interacting neighbor atoms and β_o is the exchange integral between the 5p AO's of the two Xe atoms directed along the i - j

bond. The simple expression (25) is valid only for small exchange integrals β_o , which is just the case for Xe atoms. Using the simple MO model for the Xe_2^+ molecule, one obtains

$$\beta_o = \frac{1}{2}(^2\Sigma_u - ^2\Sigma_g^+) , \quad (26)$$

where $^2\Sigma_u$ and $^2\Sigma_g^+$ are the ground state and the first excited potentials of the Xe_2^+ molecule, respectively. Using the ab initio potentials without spin-orbit coupling, which are close to the experimental potentials,¹¹ we can interpolate the numerical values of β_o by means of the exponential function

$$\beta_o(R) = -172\exp[-1.45R] , \quad R \geq 3.0 \text{ \AA} . \quad (27)$$

It is reasonable to assume that in the $\text{Xe}_{12}^+\text{Cl}^-$ system the positive charge resides on only the 12 Xe atoms surrounding the Cl^- ion, so that each of these atoms is coupled with only four other atoms. Putting $n = 4$ in the expression (25), one obtains the energy of delocalization of the $\text{Xe}_{12}^+\text{Cl}^-$ system as

$$\epsilon_v(R) = 2\beta_o(R) . \quad (28)$$

Using $V_{\text{Xe}^+\text{Cl}^-} = 4.75 \text{ eV}$ and $\beta_v(\ell) = -0.30 \text{ eV}$, we find that the energy of the formation of the symmetric $\text{Xe}_{12}^+\text{Cl}^-$ system is $V_{\text{Xe}_{12}^+\text{Cl}^-}(\ell) = 4.15 \text{ eV}$ (Fig. 3).

The activation energy of the $\text{Xe}_{12}^+\text{Cl}^-$ complex lies inside the band of the Xe^+Cl^- activation complex energy. Consequently, the excitation energy of the ionic system forms a broad band, both of whose lower and upper limits (3.94 eV and 4.75 eV) are determined by the Xe^+Cl^- excitation (Fig. 4)

We have considered the $\text{Xe}_{12}^+\text{Cl}^-$ system as an activated complex with the Xe-Cl distance $\ell = 4.38 \text{ \AA}$. As the Xe atoms in $\text{Xe}_{12}^+\text{Cl}^-$ are attracted to the Cl^- ion, they can be shifted towards the Cl^- ion. However, there are two

alternative channels for this shift. The first, which was considered in the previous section, is the shift of two Xe atoms with the formation of the Xe_2^+Cl^- molecule. The energy of the formation of this molecule in the Xe solid was proven to be equal to $V_{\text{Xe}_2^+\text{Cl}^-}^{(s)} = 3.66$ eV. The second possible channel is the symmetric shift of all 12 Xe atoms and the formation of the quasistable $\text{Xe}_{12}^+\text{Cl}^-$ system with the Xe-Cl distance smaller than the initial $\ell = 4.38$ Å. The energy of such a system is

$$V_{\text{Xe}_{12}^+\text{Cl}^-}^{(s)}(r) = I_{\text{Xe}} - A_{\text{Cl}} + U_{\text{Xe}_2^+\text{Cl}^-}^{(g)}(r) + 11\bar{U}_{\text{XeCl}^-}(r) - 12U_{\text{XeCl}}(\ell) + U_{\text{Xe}_{12}^{\text{M}}}(r) - U_{\text{Xe}_{12}^{\text{M}}}(\ell) + \epsilon_p(r) + \epsilon_v(r), \quad (29)$$

where $U_{\text{Xe}_{12}^{\text{M}}}$ is the interaction of the 12 Xe atoms with the Xe matrix and one with another. According to the results of our calculations (Fig. 4), the energy (29) has a minimum at the point of $r_m = 4.03$ Å with the energy of stabilization [relative to the initial $V_{\text{Xe}_{12}^+\text{Cl}^-}(\ell)$] of 0.54 eV. The energy (29) at its minimum is $V_{\text{Xe}_{12}^+\text{Cl}^-}(4.03) = 3.61$ eV. This value is lower than the energy of the Xe_2^+Cl^- molecule (3.66 eV). However, the difference is too small to imply that the $\text{Xe}_{12}^+\text{Cl}^-$ system is more stable in the solid phase than the Xe_2^+Cl^- molecule.

The energy of the transition in the $\text{Xe}_{12}^+\text{Cl}^-$ system,

$$T_{\text{Xe}_{12}^+\text{Cl}^-} = V_{\text{Xe}_{12}^+\text{Cl}^-}^{(s)}(r_m) - V_{\text{Xe}_{12}^+\text{Cl}^-}^{(s)}(r_m), \quad (30)$$

is found to be equal to 3.89 eV ($\lambda = 319$ nm), which is too far from the experimentally observed $\lambda = 570$ nm.⁷ At the same time, the calculation performed in the previous section confirms that Xe_2^+Cl^- is responsible for

the emission at $\lambda = 570$ nm. It follows that Xe_2^+Cl^- rather than $\text{Xe}_{12}^+\text{Cl}^-$ is really the most stable ionic system in the Xe solid.

One of the assumptions of the present calculation is the neglect of the valence interaction between the Xe atoms of a molecule and the matrix atoms. Using the Xe^+ -Xe resonance integral (27), it is possible to estimate the error resulting from this neglect. Let us consider the Cl^- ion and three neighboring Xe atoms with a common +1 charge. Two of these Xe atoms and Cl^- ion belong to the molecule whereas the third Xe atom belongs to the matrix and is located farther from the Cl^- ion. Taking into account only the Coulomb Xe^+-Cl^- interaction, we find the valence interaction with the third Xe atom to be on the order of 0.1-0.15 eV. It follows that ignoring the molecule-matrix valence interaction, we have made an error which is not negligibly small; however, it is also not large enough to significantly change the results of the calculations.

VI. Conclusion

1. The energies of ionic xenon-chlorine systems in a solid Xe matrix have been calculated in order to study their optical properties and stability. The calculation takes into account the electrostatic polarization of the matrix and the repulsive and van der Waals interactions between all pairs of atoms involved (Xe-Xe , Xe-Cl , Xe-Cl^-). The known potentials of these interactions have been interpolated by analytical expressions.

2. The calculation of the energy levels of the Xe_2^+Cl^- ionic molecule in the Xe matrix strongly supports the hypothesis that these molecules are responsible for the emission of $\lambda = 570$ nm light observed experimentally.⁷ The calculated wavelength of the Xe_2^+Cl^- optical transition is $\lambda = 540$ nm.

While the shift of the transition wavelength in the solid matrix compared to the gas-phase value ($\lambda = 484$ nm) is mainly due to the polarization of the Xe matrix by the Xe_2^+Cl^- molecule, the van der Waals interactions are also of importance.

3. The calculation of the energy of the activation complexes Xe^+Cl^- and $\text{Xe}_{12}^+\text{Cl}^-$ reveals that the excitation energy needed for the radiative formation of the Xe_2^+Cl^- ionic molecule lies in an interval between 3.94 eV and 4.75 eV.

4. The possibility of formation of an ionic complex $\text{Xe}_{12}^+\text{Cl}^-$ in the solid Xe has been investigated. The calculated energy of this complex is slightly lower than the energy of the Xe_2^+Cl^- ionic molecule. However, the transition energy of the $\text{Xe}_{12}^+\text{Cl}^-$ complex is much higher than the experimentally observed value, so that most probably the $\text{Xe}_{12}^+\text{Cl}^-$ complex is actually unstable relative to the Xe_2^+Cl^- molecule.

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TABLE 1Coordinates of Some of the Xe Atoms in the Xe_2Cl^- Solid System

<u>i</u>	<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>
0	Cl^-	0	0	0
1	$\text{Xe}^{1/2+}$	2.33	2.33	0
2	$\text{Xe}^{1/2+}$	2.33	0	2.33
3	Xe	0	3.10	3.10
4	Xe	-3.10	3.10	0
5	Xe	-3.10	0	3.10
6	Xe	0	-3.10	3.10
13	Xe	6.19	6.19	0
14	Xe	6.19	3.10	3.10
15	Xe	3.10	6.19	3.10
16	Xe	0	6.19	0

Figure Captions

1. Lowest-lying potential energy states of XeCl (adapted from Ref. 2)
illustrating the photoassociative production of electronically excited XeCl and subsequent fluorescence of the excimer at 350 nm on the C $\rightarrow$ A band. The binding of the ground state has been exaggerated for clarity.
2. Diatomics-in-molecules potential surfaces for Xe₂Cl leading to Xe₂ + Cl⁻ (adapted from Ref. 10).
3. Schematic presentation of the energy levels and transitions in the Xe₂⁺Cl⁻ molecule (see text). The numbers stand for energies in eV.
4. Energy levels of the ionic systems Xe₂⁺Cl⁻, Xe₁₂⁺Cl⁻ (potential curve), and Xe⁺Cl⁻ relative to the neutral Cl + Xe solid system.

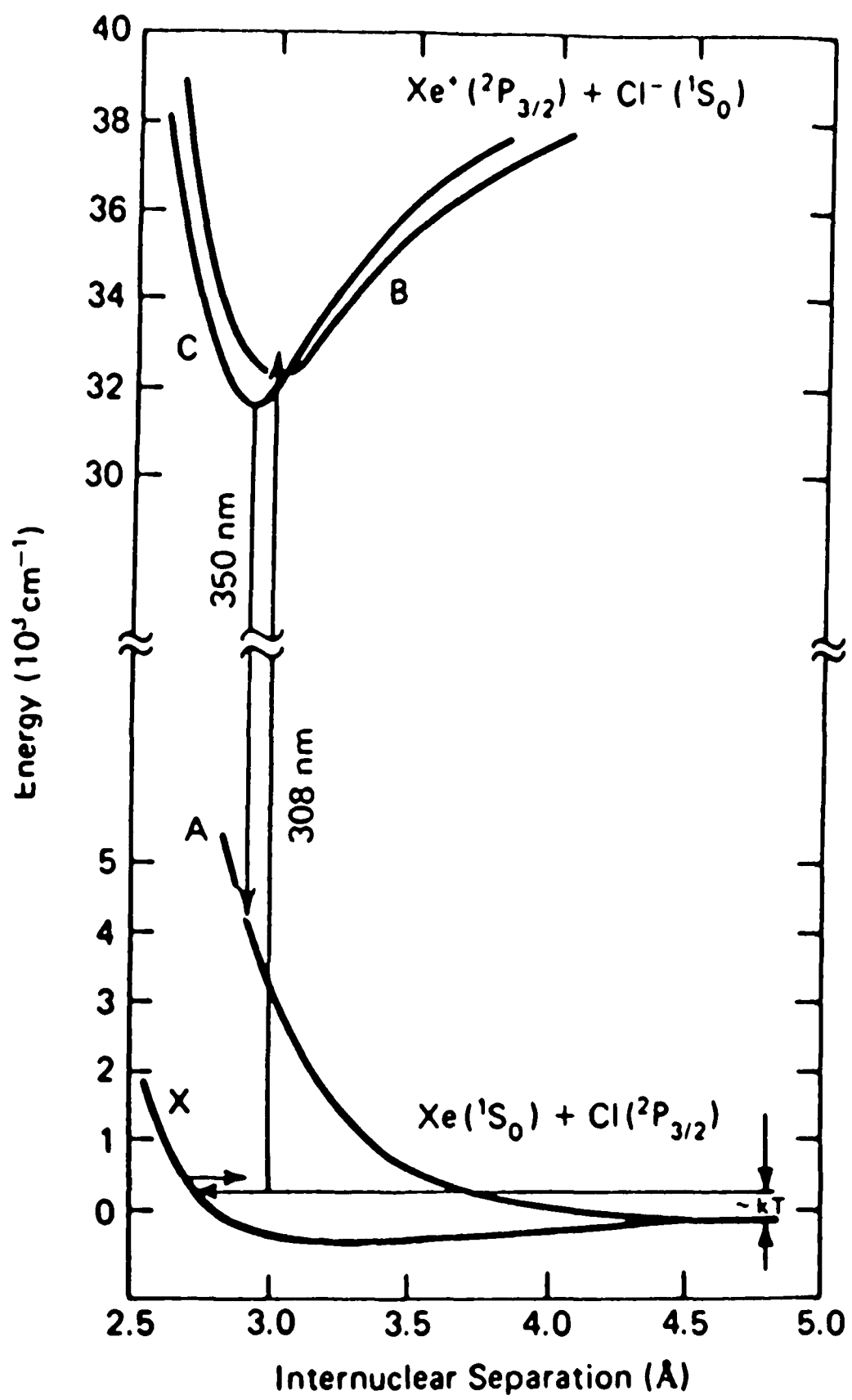


Fig. 2

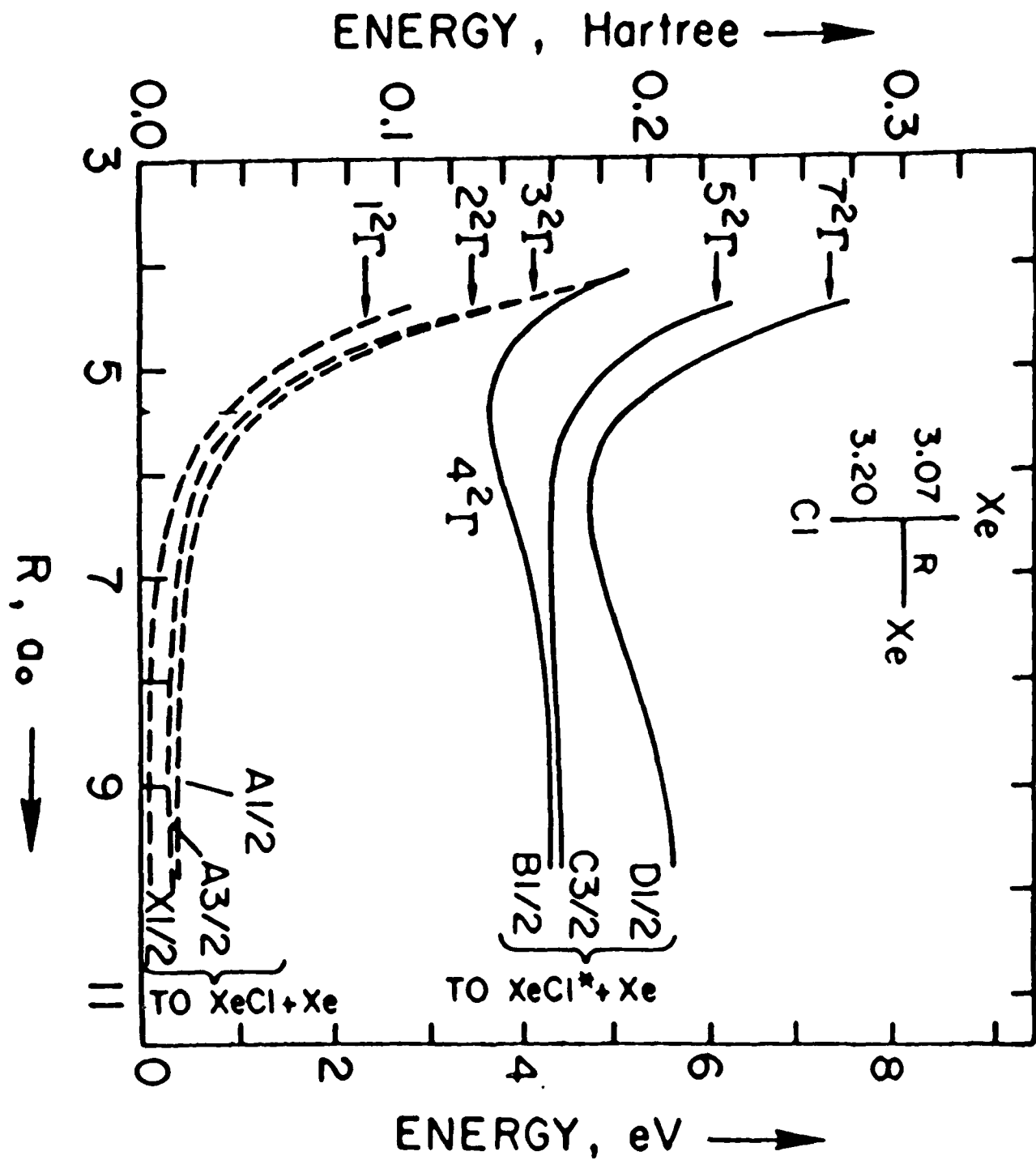


Fig 3

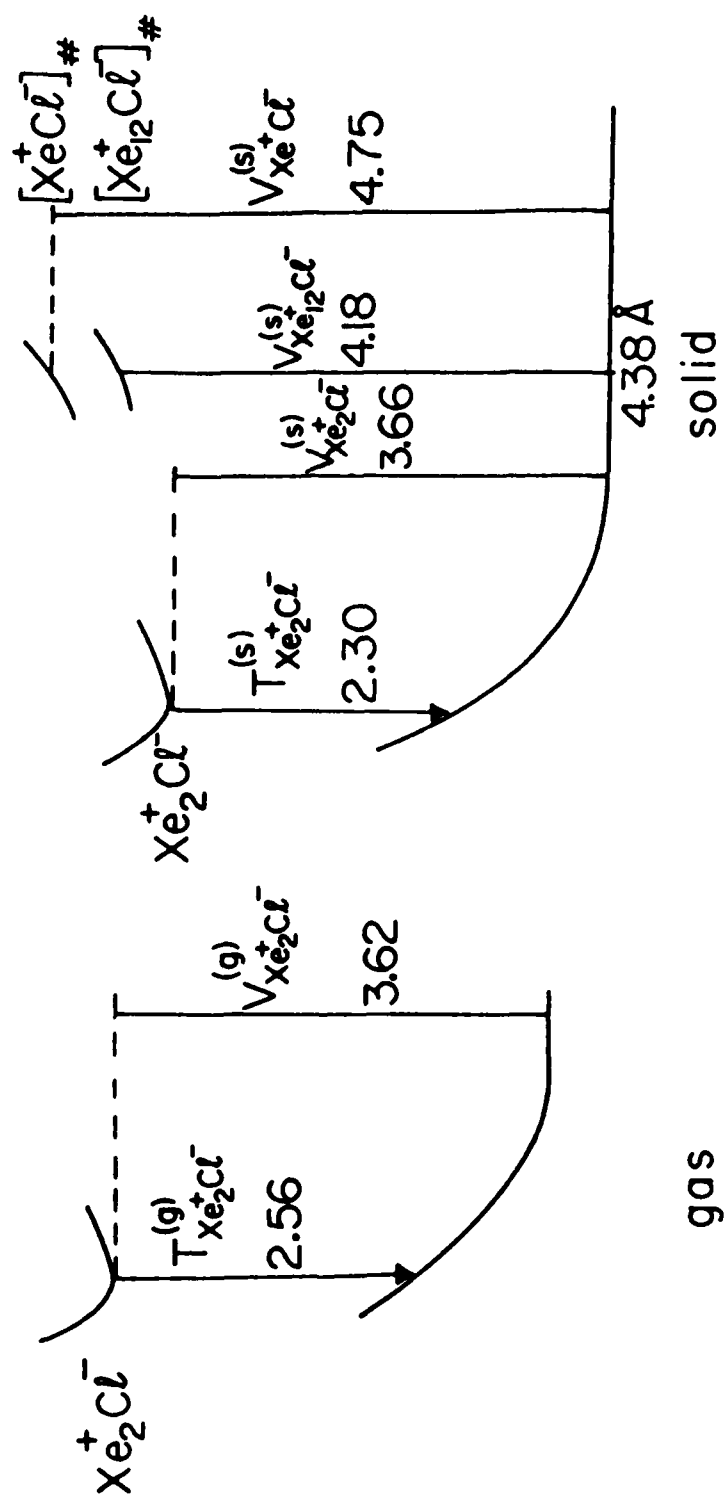
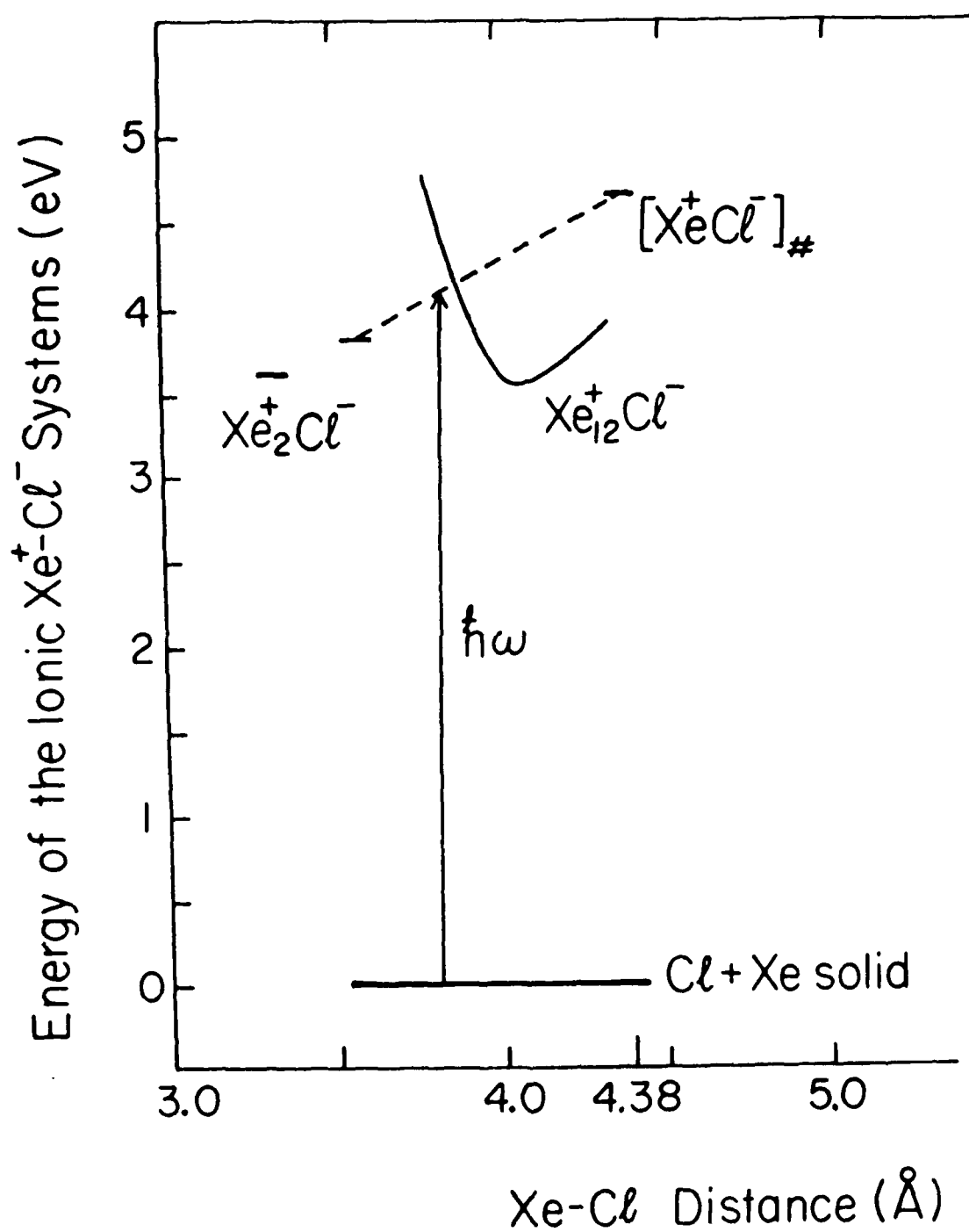


Fig. 4



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