

X-ray photoelectron spectroscopy of gaseous and solid I_2 : Ion-state-enhanced intermolecular interactions

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Gas- and solid-phase x-ray photoelectron spectra of I_2 are compared. The shake-up satellite structure on the core-level peaks for I_2 in the gas phase can be interpreted using a one-electron model of electronic transitions among states of the molecular ion. In the solid phase, the shake-up transition energies are greatly increased owing to the dynamic nature of the photoionization process, which enhances the intermolecular interactions of the molecular ion with neighboring neutral molecules. Complete-neglect-of-differential-overlap-2 model molecular-orbital calculations have been used to interpret the spectra in terms of strong intermolecular interactions in the solid phase.

I. INTRODUCTION

The optical-absorption spectra of I_2 molecules in the gas phase are among the most extensively studied molecular spectra.¹ Many ultraviolet photoelectron spectroscopic (UPS) studies also have been reported which focus mainly on the large spin-orbit interaction in I_2 molecules (in the gas phase).²⁻⁵ Only very few x-ray photoelectron spectroscopy (XPS) studies have been reported. These XPS studies focus mainly upon the many-body effects in the $4s$ and $4p$ core-level spectra,⁶⁻⁹ as well as the tabulation of the other core-level binding energies in order to facilitate the interpretation of many-electron effects in electron-beam-excited Auger spectroscopy.¹⁰ In this paper we report the results of a study of the shake-up satellites on XPS core-level peaks of I_2 molecules in the gas as well as the condensed phase, and interpretation in terms of enhanced intermolecular interactions in the solid due to the dynamics of the photoionization of I_2 .

In the course of acquiring reference XPS spectra for a study of I_2 -doped polyacetylene,¹¹ we observed shake-up satellites on the XPS core-level peaks of I_2 molecules in the gas phase which were dramatically different than those we observed for I_2 molecules in the condensed molecular solid spectra. Some preliminary I_2 XPS spectra were presented in the course of reporting the I_2 -doped polyacetylene results.¹¹ We also found that some features of the XPS valence band were different for I_2 molecules in the condensed molecular phase as compared with I_2 in the gas phase. In this paper, we report the results of a subsequent study of the XPS spectra of I_2 molecules, and an explanation of the energies and intensities of the shake-up peaks for both the gas and solid phases.

The strong intermolecular interactions that occur in solid I_2 are modeled using a complete-neglect-of-differential-overlap-2 (CNDO/2)-level molecular-orbital (MO) scheme. These MO results are in accord with the experimental observations. In fact, the presence of strong intermolecular interaction effects in the photoelectron spectra of solid iodine could be anticipated, since such diverse measurements as optical-absorption spectroscopy¹² and photogenerated electronic transport studies¹³ indicate more-or-less-conventional semiconducting behavior, rather than behavior normally associated with molecular solids. We report that the process of photoemission serves to intensify the intermolecular interactions. That is, the interaction of the molecular ion, created by photoionization, with the surrounding neutral iodine molecules results in prominent structure in the XPS spectra.

II. EXPERIMENTAL

The starting material used in this study was as-received J. T. Baker reagent-grade I_2 . No impurity lines were detected in either the solid- or gas-phase XPS spectroscopy, with the sole exception of a weak apparent core-level-like doublet peak at about 30 eV (relative to the vacuum level) in the gas-phase spectra *only*. No related XPS, satellite or Auger peaks could be detected for logical impurities that might have resulted in the anomalous signal, however. Photoelectron spectra were recorded using only unfiltered Mg $K\alpha$ radiation (1253.7-eV photon energy) and a standard AEI ES 200B photoelectron spectrometer.

Gas-phase data were recorded at about $+50^\circ\text{C}$ using the standard AEI gas-cell component. The spectrometer analyzer pressure was maintained below 2×10^{-5} Torr (gauge) to avoid electron-molecule collisions. The spectrometer source-chamber pressure was maintained in the low 10^{-5} -Torr (gauge) range in order to minimize electron-molecule collisions in the *gas-cell* chamber (estimated pressure 0.1 Torr). The pressure dependence of the various core-level intensities was used to set the pressure at an appropriate low value.⁶ At higher pressures, some pressure-dependent effects were observed, which will be discussed below.

Solid-phase spectra were recorded by subliming I_2 at room temperature on to clean gold substrates at -100°C . The Au 4*f* levels were recorded during vapor deposition. Deposition was terminated as soon as the Au 4*f* signal disappeared due to the presence of the I_2 overlayer. The advantages inherent to this technique have been fully discussed previously.¹⁴

III. RESULTS

The valence XPS spectra are shown in Fig. 1, along with the published UPS gas-phase data of Potts and Price,⁴ and a schematic atomic-orbital representation of the one-electron initial states, from which electrons originate, that give rise to the peaks in the photoelectron spectra.

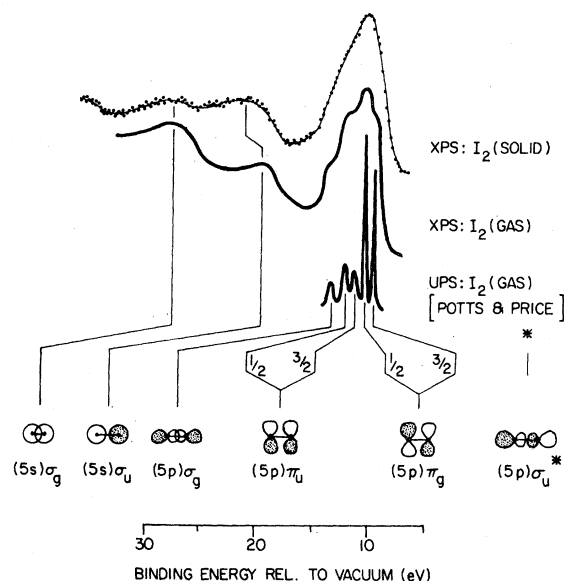


FIG. 1. XPS valence data for I_2 in the gas phase (middle curve) is compared with that for the condensed I_2 (data points, upper curve) and the HeI UPS data of Potts and Price (Ref. 4) (lower curve) of I_2 in the gas phase. The energy scale is that for the gas-phase spectra. Energy referencing is discussed in the text. The splitting of the π states is due to the strong spin-orbital coupling in iodine (Ref. 3).

toelectron spectra. Various investigators have characterized the symmetries of the orbital sequence as shown.²⁻⁵ The ionization potentials (IP's) corresponding to the $15s$ -derived MO's however, do not seem to have been reported previously. Note that the maxima in the photoelectron peaks corresponding to the removal of an electron from the $5s\sigma_g$ or $5s\sigma_u$ one-electron levels have a different spacing in the solid as compared with the gas-phase spectra. Many-body effects may, however, lead to this apparent difference, as will be discussed below.¹⁵ The solid-phase spectra were positioned in Fig. 1 by aligning

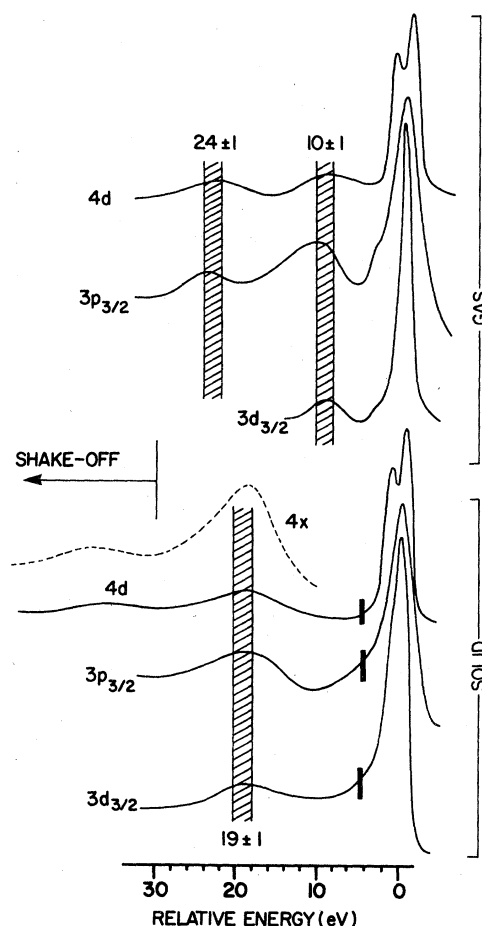


FIG. 2. Lower kinetic energy side of the $13p_{3/2}$, $13d_{3/2}$, and $14d_{1/2,3/2}$ peaks are shown for I_2 in the gas phase and condensed-molecular solid I_2 . The kinetic energies are about 380, 620, and 1200 eV, respectively. The 19-eV satellite on the $13d_{5/2}$ spectrum would appear at about 10 eV on the $13d_{3/2}$ curve, and influences the 10-eV peak. For the solid-phase data, where better statistics are obtained, and the shake-off can be recorded, the first moment of the total intensity distribution $M_1 = \sum_i I_i E_i / \sum_j I_j$, is indicated by a bar. The bars represent the Koopmans energies, i.e., the binding energies relative to the main peak of the given core levels in the neutral molecule.

TABLE I. Satellite intensities. (FWHM is full width at half maximum.)

Phase	Iodine core level	Small satellite		Large satellite 1			Large satellite 2		
		Energy ^a	Intensity ^b	Energy ^a	Intensity ^b	FWHM	Energy ^a	Intensity ^b	FWHM
Gas	4 <i>d</i>			9	18	6	23	11	7
	3 <i>d</i> _{3/2}	4	4	9	16	5			
	3 <i>p</i> _{3/2}	4	3	11	22	10	24	9	8
Solid	4 <i>d</i>			18	23	10			
	3 <i>d</i> _{3/2}			19	23	10			
	3 <i>p</i> _{3/2}			18	24	8			

^aEnergy relative to centroid of main core-level peak, in eV, ± 1 eV.^bPercentage of total intensity.

the major feature of the gas- and solid-phase curves. These spectra would otherwise appear offset in energy, even when only the normal (weak) van der Waals intermolecular relaxation energy effects¹⁶⁻²¹ are present (typically 1 to 2 eV), but also because the gas-phase data are recorded relative to the Fermi level.⁵ The absolute energy scale, relative to the vacuum level, for the UPS data are taken from Potts and Price,⁴ while that for the XPS data were fixed by recording the N 1s level of N₂ for reference and using Siegbahn's value⁶ of 409.5 eV. With this reference procedure, the first major peak in the XPS spectrum lines up precisely with the set of $\pi_{g3/2}$, $\pi_{g1/2}$ peaks of the UPS spectrum.

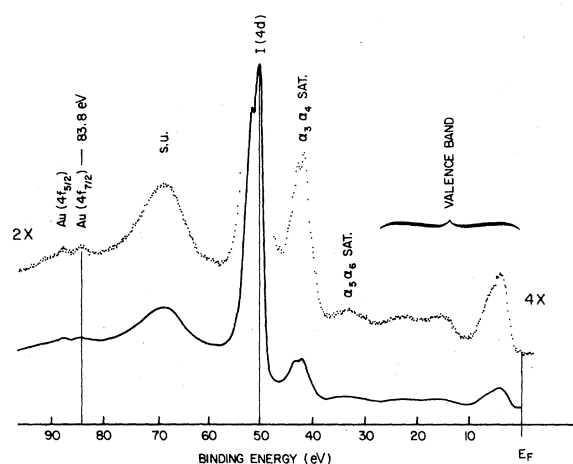


FIG. 3. Wide scan of the valence and 4*d* region for condensed-molecular solid I₂ is shown. The right-hand portion is also shown expanded in the intensity direction by 4 $\times$, while the left-hand portion is shown expanded by 2 $\times$. Note that the 18-eV shake-up peak is about two times the integrated valence-spectrum intensity. Also, a weak Au 4*f*_{5/2, 7/2} doublet can be seen from the substrate. This Au signal has been used to calibrate the binding-energy spectrum, with the Au 4*f*_{7/2} peak taken to be 83.8 eV.

In Fig. 2 is shown the low kinetic energy (shake-up or su) satellite peaks associated with various iodine core-level lines for both the gas and condensed phases. In the gas-phase data shown, the I 3*p*_{3/2} line and the I 4*d* line have two major apparent su satellites at about 11 and 24 eV (± 1 eV) relative to the main peak. The I 3*d*_{3/2} line has only one major su satellite, weaker in intensity, at about 9.5 eV (± 1 eV) relative to the main peak. In the solid-phase data, however, all of the core-level lines have only a broad satellite feature near 19 eV, while on the I 4*d* line, we can detect a second, much weaker, broad structure at 38 eV. These spectra are tabulated in Table I. Note that many-body effects in the form of super Coster-Kronig effects associated with the removal of an electron from a 4*s* or 4*p* core level have been studied previously.^{6-9, 22} We have avoided inclusion of these spectra for this reason. We interpret the differences between the gas- and condensed-phase XPS spectra of I₂ as due to strong intermolecular interactions within the solid.

In Fig. 3 is shown a wide scan of the lower-binding-energy portion of the condensed I₂ spectra. From this figure one can get an idea of the relative intensities of the shake-up on the I 4*d* line as compared with the valence region intensity. The weak Au 4*f* peaks are used in the energy calibration procedure.

IV. DISCUSSION

A. Conceptual background

The peaks in a photoelectron spectrum of an isolated molecule, correspond to the states of the photoionized molecular-ion containing $N - 1$ electrons. The main peak, the one usually at lowest binding energy and with the largest intensity, corresponds to the lowest-energy state of the ion with a hole (absence of

an electron) in a given core-electron shell or a valence molecular-orbital level. The satellite peaks on the low kinetic energy (high-binding-energy) side of the main peak, then correspond to higher-energy $N - 1$ electron states of the molecular ion, for the hole in a given molecular energy level. These satellite peaks correspond to real many-electron effects associated with the photoemission process. These satellite peaks can be rationalized, however, on a one-electron basis in limiting cases.²³ In the context of a one-electron formalism, the satellite peaks correspond to electronic transitions from occupied one-electron molecular orbitals into the unoccupied molecular orbitals (so-called shake-up transitions) or into the continuum (so-called shake-off transitions). These latter, shake-off transitions correspond to double ionization of the initially neutral molecule. In the sudden approximation, it has been shown that the first moment of the core-level spectral energy distribution, M_1 , is equal to the energy of the corresponding one-electron state in the neutral molecule.²⁴ Thus it has become increasingly important to understand the total spectral energy distribution that appears upon photoemission of an electron from a given molecular level, in order to address chemical shifts of that level in the neutral molecule. These shifts correspond to energy differences between the relevant M_1 's, rather than just between the main photoemission peaks.^{23,24}

In comparing the gas- and solid-phase data in Fig. 2, the centroid of each main feature is aligned with the zero point on the energy axis in order that the subpeak energies can be compared. There are apparent differences in the solid-phase binding energies, as compared with the gas-phase binding energies, however. These differences have been shown to be due to the interaction of the hole state, photogenerated on a given molecule in the molecular solid, with those portions of the frequency-dependent elementary excitation spectrum (dielectric function) of the surrounding molecular solid to which the hole state is weakly coupled.^{19,25} Strong-coupling branches, on the other hand, lead to a temperature-dependent broadening of the photoelectron peak. The gas-to-solid main-peak energy shifts can be estimated. The gas-phase spectra are referenced to the vacuum level, while the solid-phase spectra are relative to the Fermi level, however. We must first reference both sets of spectra to the same energy scale. The work function of the clean gold substrate was measured to be 5.0 eV. Although the spectra of condensed I_2 (insulating film) will not exhibit a sharp E_F , the Fermi level of the film will, however, align with that of the gold substrate, since we only consider films ~ 100 Å thick to eliminate sample charging problems.¹⁴ Thus the I_2 spectra obtained on the gold substrate can be referenced to the vacuum by observing the cutoff of the secondary electron spectrum, adding the photon ener-

gy and subtracting the energy of the Fermi level of the gold substrate (since the Fermi levels align and the Fermi level of I_2 is not directly observable with photoemission). The uncertainty thus introduced in the present case is about ± 0.5 eV. There then remains a difference of $\Delta E = 2.2 \pm 0.5$ eV, between the gas- and solid-phase spectral features, which is termed the intermolecular polarization energy, or alternatively, the intermolecular relaxation energy.^{16,18} A typical value is $\Delta E = 1.5 \pm 0.3$ eV in most molecular solids.¹⁶ Thus even this aspect of our photoemission results indicates that I_2 exhibits significantly stronger intermolecular interactions than typical molecular solids, a conclusion directly indicated by the respective relaxation energies (i.e., $\Delta E = 1.5$ vs 2.2 eV).

In a one-electron picture, the first moment of the intensity distribution of core-level k (including satellite features),

$$M_1^k = \sum_i I_i^k E_i^k / \sum_j I_j^k, \quad (1)$$

is equal to the binding energy of the levels k in the neutral molecule (i.e., Koopman's value).²⁴ It is this value, M_1^k , rather than the binding energy of the main photoelectron peak, E_k^0 , to which chemical-shift analysis should be applied when comparing XPS spectra of different materials, especially when the structure differs between two spectra of the same energy level.²³ In Fig. 2(b) the vertical bar on each spectrum represents the first moment of that spectrum. To within experimental error, the energy differences between M_1 's and the main photoelectron peaks are equal to about 4.5 eV, because the shake-up features are approximately the same in each spectrum. The first moments for the gas-phase spectra are not shown. There is more scatter in the M_1 's for the gas phase, which we believe is due to poorer statistics in the gas-phase spectra. Averaging the computed M_1 's for the gas-phase spectra, however, a (4.5 ± 0.5) -eV difference in energy between M_1 and the centroid of each main photoemission peak is obtained, which is consistent with the value in the solid phase. Thus the intensity in the su spectrum in the solid is redistributed relative to that in the gas phase, but the first moment of the distribution appears to be unchanged. Thus the gas-to-solid relaxation energy shift is about 2.2 eV as taken from the main-line energy differences or from the first-moment energy differences. The second moment of the distribution has recently been discussed,²⁶ but its utility remains to be established.

In a recent paper, we have compared the shake-up excitations observed in XPS core-level spectra of a series of diatomic molecules (molecular-ion spectra), with optical excitations observed in the neutral molecules.²³ We presented arguments why this simple analysis can be applied to the spectra of certain

small molecules. In Secs. IIIB and IIIC of this paper, we apply the same analysis to I_2 molecules in the gas phase. Then we utilize a CNDO/2 formalism to model the intermolecular interactions in solid iodine. First the energies of the shake-up peaks, then the relative intensities are discussed. In each case, a comparison of the gas-phase results with corresponding solid-phase XPS spectra is made.

B. Shake-up energies: Gas phase

The two basic conditions for rationalizing shake-up spectra on the basis of optical-absorption spectra of the neutral molecule are^{23,27} (1) the electronic screening in the presence of the core hole should be such that only small differences occur between the low-energy one-electron transitions involving the outer valence molecular orbitals in the neutral molecule and those in the molecular ion; and (2) the configuration interaction leading to energy separation between different final states resulting from the same one-electron transition should be similar.

Figure 4 shows a comparison of the excitation energies of the I_2 molecule in the gas phase: the row labeled " $N-1$ " shows the mean energies of the shake-up satellites observed in the XPS 4*d* spectrum; and the row labeled " N " contains information on those excitations in the neutral I_2 molecule which are in the same energy region as the shake-up peaks.¹ In the neutral molecule, the $\sigma^* \leftarrow \sigma$ excitation (~ 6.9 eV) and the $\pi^* \leftarrow \pi$ excitation (~ 2.5 eV) are indicated by solid lines. The triplet states resulting from the same excitation are shown as broken lines. The lowest-energy excitations (up to about 10 eV) are smaller by about 2.5–3 eV in the neutral molecule (row N) relative to the molecular-ion excitation energies (row $N-1$). This energy difference is due to the different electronic screening (relaxation) effects in the neutral molecule relative to the ion, as discussed previously.²³

In order to demonstrate the screening effect for a

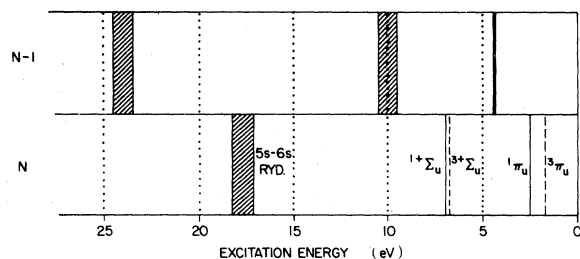


FIG. 4. Row labeled ($N-1$) shows the high-energy electronic excitations in the I_2 molecular ion, while the row labeled (N) shows the energies of the same transitions in the neutral molecule I_2 , as taken from Mulliken and Person (Ref. 1).

halogen molecular ion, we have carried out CNDO/2-level calculations²⁸ of the one-electron energy levels of the Cl_2 molecule. Chlorine is the heaviest halogen for which good CNDO/2 parameters are available to us. These model calculations merely serve the purpose of illustrating the general trends, since no attempt was made to fit or reproduce experimental values accurately. Figure 5 shows some results of the calculations on Cl_2 , where the presence of a core hole in the column labeled " $N-1$ " has been stimulated within an equivalent-cores ($Z+1$) approximation.^{29,30} The presence of the core hole stabilizes (increases the binding energy of) the occupied orbitals more than it does the unoccupied orbitals. This stabilization effect increases the transition energies accordingly, as indicated by the $\Delta(\Delta E')$ values in the lower portion of the figure. In general, the higher the binding energy of a given orbital (the more inner valence-like), the stronger is the stabilization effect.

The trend presented in the previous paragraph is basically in agreement with experiment, enabling the conclusion that in the gas-phase data of Fig. 2, the shake-up peak near 10 eV is due to $\sigma^* \leftarrow \sigma$ transitions and the weak shoulder near 4.5 eV is due to $\pi^* \leftarrow \pi$ excitations. It is not obvious, however, that these are the only transitions that contribute to these

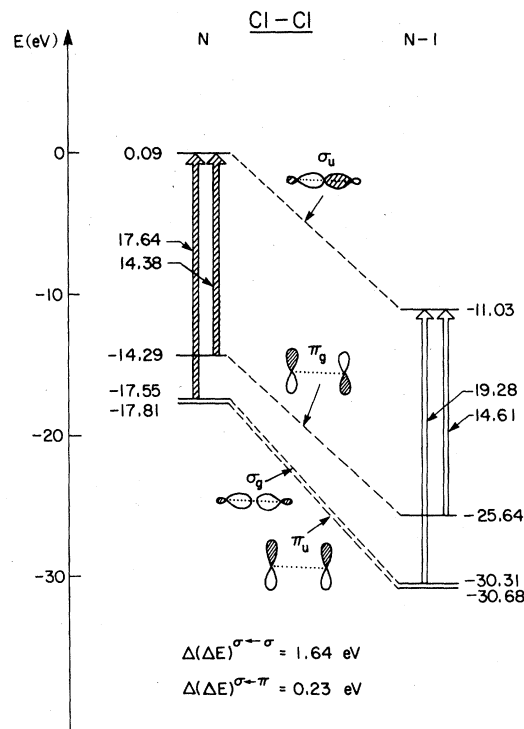


FIG. 5. Upper two occupied and lowest-energy unoccupied molecular-orbital energies of the neutral Cl_2 molecule are compared with those levels in Cl_2^+ containing a core hole using a CNDO/2 formalism.

peaks. Indeed, there is reason to believe that additional transitions due to multiple excitations³¹ from both π orbitals and σ levels can occur under the broad peaks observed.

The feature near 24 eV, relative to the main peak, is more difficult to address. Optical data do not exist in this energy region. The only available work is that by Comes, Nielsen, and Schwarz³² who used soft-x-ray absorption to study 4*d*-core excitons. They find evidence for a Rydberg-type (σ_g) state about 5 to 6 eV above the $5p\sigma_u^*$ orbital energy. There are several indications that transitions to this Rydberg state are responsible for the 24-eV shake-up structure. The initial state involved corresponds to the $5s\sigma_u$, in our valence spectrum shown in Fig. 1, which lies about 10 eV below the highest occupied molecular orbital (HOMO). With the $5p\sigma_u$ about 2.5 eV above the HOMO, we have an orbital difference of about 18 eV. The screening effects discussed elsewhere²³ and referred to above, which are larger for the inner-valence levels, then account for the remainder of the energy difference, i.e., about 6 eV.

One might argue that the 24-eV peak could be due to double ionization processes, i.e., shake-off. However, estimates of the double ionization threshold from core-level binding energies and the Auger spectroscopy thresholds, as reported recently by Aksela, Aksela, and Thomas,¹⁰ indicate a shake-off threshold of about 30 eV, well outside the region of the 24-eV shake-up peak.

Finally, at increased I_2 pressures in the gas-cell energy-loss effects are observed. In the process of increasing the pressure to about 15 times that at which the data presented here were taken, however, we observe the 10-eV peak begin to shift toward higher excitation energy. Thus the I_2 molecular collisions already are shifting the 10-eV peak toward its position in the solid, near 18 eV, as discussed below.

C. Shake-up energies: Solid Phase

The Solid I_2 XPS shake-up spectra and valence spectrum are considerably different from the gas-phase counterparts. In the valence spectrum, the lower-lying peaks are smeared together due to solid-state linewidth effects.¹⁶⁻¹⁹ These effects leading to the large linewidths in molecular solids have been discussed previously.¹⁹ For the I_2 molecules condensed, the maximum in the photoelectron peak corresponding to the $5s\sigma_u$ level seems deeper in binding energy, relative to the remainder of the valence spectrum, than it was in the gas-phase valence spectrum. Also, in the core-level spectra there are still two satellite peaks, but now at about 18 and 36 eV. This latter peak lies above the 30-eV threshold for double ionization and is thus likely due to shake-off transitions. We believe these transitions are not observed in the gas phase due to the low counting rates which

lead to poorer statistics in the gas-phase spectra.

In order to address the 18-eV shake-up peak, we resorted to CNDO/2 calculations of the chlorine trimer, $(Cl_2)_3$, using the dashed outlined portion of the solid iodine-crystal geometry, as shown in Fig. 6, as a guide. The $(Cl_2)_3$ geometry allows an approximation of the intermolecular interactions, which have been shown previously³³ to perturb the intermolecular charge distributions in solid I_2 . Also, Bersohn³⁴ and later Rosenberg³⁵ have shown that it is basically the interaction between σ orbitals on a given molecule with π orbitals on adjacent molecules that is responsible for the strong interaction. One manifestation of these large intermolecular interactions in solid I_2 is the large value of the heat of sublimation, 15.66 kcal/mol; a value equal to about 43% of the dissociation energy of gaseous I_2 at 0 K.³⁶ The large value has been explained through a σ - π -interaction mechanism,³⁵ which we show leads to an effect in the excitation spectrum in the presence of a core-hole (shake-up spectra).

Our analysis is based upon an idea proposed by Mulliken for charge transfer interactions.³⁷ The antibonding orbital, into which an electron is promoted in a $\sigma^* \leftarrow \sigma$ transition, is much more diffuse than the bonding orbital.³² The surrounding molecules stabilize the $5s\sigma_u$ level (with a hole in it) by about 2 eV as seen in the valence excitation by which an electron is put into the σ_u^* level in the presence of the core hole, the electronic charge density increases its spatial extent. The consequent increase in the repulsion energy between it and the neighboring molecules in the

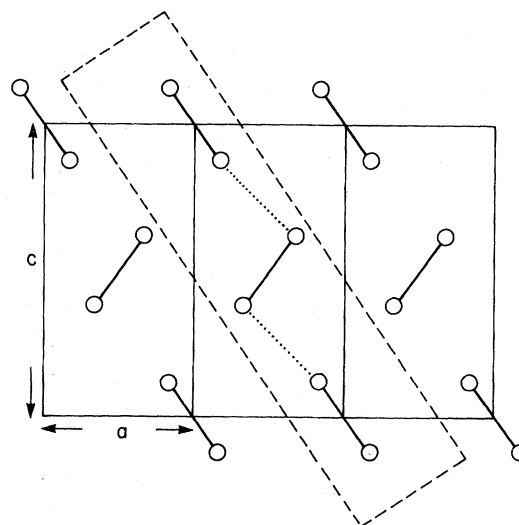


FIG. 6. Solid I_2 crystal geometry after A. I. Kitaigorodskii, T. L. Khotsyauora, and Y. T. Struchkov [Zh. Fiz. Khim. 27, 780 (1953)]. The dashed line shows the positions of the three molecules used in the CNDO/2 modeling of the I_2 intermolecular interactions.

crystal, must be added to the excitation energy that is otherwise observed in the gas-phase molecule.

In Fig. 6 is shown the arrangement of I_2 molecules in the solid. The portion of the system to be studied with the $(Cl_2)_3$ trimer is shown outlined by a dashed line. This set of three diatomic molecules is sufficient to exhibit the intermolecular interaction effects we are after, at least in a qualitative way, as shown previously in a study of solid-state effects in paraniroaniline.^{20,21} Some details of the interaction scheme are shown in Fig. 7, in terms of a schematic molecular-orbital diagram. The symmetry of the $(Cl_2)_3$ system shown is C_{2h} . The two outer halogen molecules, which serve to approximate the role of the iodine lattice, are positioned relative to the central I_2 molecule at an angle of 130° . It is conceptually straightforward to first form group orbitals of the outer two "lattice" I_2 molecules, the symmetries of which are indicated in the figure. The energy spacings for the outer lattice molecules to be dimerized are those computed for the Cl_2 neutral molecule, while the energy levels for the central molecules are those computed for the Cl_2^+ ion. This allows the unoccupied σ^* orbital, stabilized by the core hole as already shown in Fig. 5, to interact strongly with occupied π orbitals of the "lattice" $(Cl_2)_2$ dimer. The interaction splitting, shown in Fig. 7, comes about since one of the combinations of molecular π orbi-

als, built out of atomic p functions, transforms as B_u and may couple to the σ^* orbital of the ion. The geometry of the crystal allows for very efficient overlap, leading to a larger shift in the solid, as shown in the upper center of the energy diagram of Fig. 7. It is obvious how this orbital shift due to solid-state interactions leads to an increase in the excitation energy as observed in the solid-state shake-up spectrum. It is this reasoning that leads us to associate the 18-eV shake-up peak in the solid I_2 core-level spectra with the same transitions which give rise to the 10-eV peak in the gas-phase core-level spectra.

At this point it is interesting to compare the photoemission results with those of the core-exciton results of Comes and co-workers.³² The fact that in the case of the core-exciton study, the valence excitation is at nearly the same energy in the solid as in the gas phase, shows that the strong shift is mostly due to the effect of creating the ion in the photoemission experiment, and not due solely to the lattice of neutral I_2 molecules. In other words, the fact that there are intermolecular interactions among the neutral molecules in solid iodine is apparent in the work of many investigators.^{1,30,32-37} Apparently, the intermolecular interactions are greater in the photoemission case by virtue of the observation of the very large energy shift of the $\sigma^* \leftarrow \sigma$ shake-up peak. Clearly the magnitude of the shift in the photoemission case is caused by the dynamics of the measurement, through the final states of the molecular ions, rather than merely by the intermolecular interactions among the neutral molecules. This explanation of the gas-to-solid shake-up peak energy differences is in line with recent analyses of XPS core-level spectra of materials systems where two components are weakly coupled in the ground state of the neutral molecule. Some examples are CO molecules adsorbed on transition-metal surfaces,³⁸⁻⁴⁰ transition-metal carbonyls,^{38,39} and molecular solids like paraniroaniline.^{20,21} In all of these cases, the dynamics of the measurement cause dramatic effects in the shake-up spectra.

Finally, as stated in Sec. IV B, at very high gas-cell pressures, we observe the 10-eV shake-up peak in the gas-phase spectra to shift toward higher excitation energies. This indicates alone that the 18-eV peak in the solid phase is likely derived from the 10-eV peak in the gas-phase data. In addition, at high pressures additional pressure-dependent structure is observed, due to electron energy-loss processes, which tend to smear out the shake-up structure. The true shake-up structure is not pressure dependent, and must be observed at lowest possible pressures.

D. Shake-up intensities

Within the sudden approximation, the intensities of a dipole transition are determined by the matrix

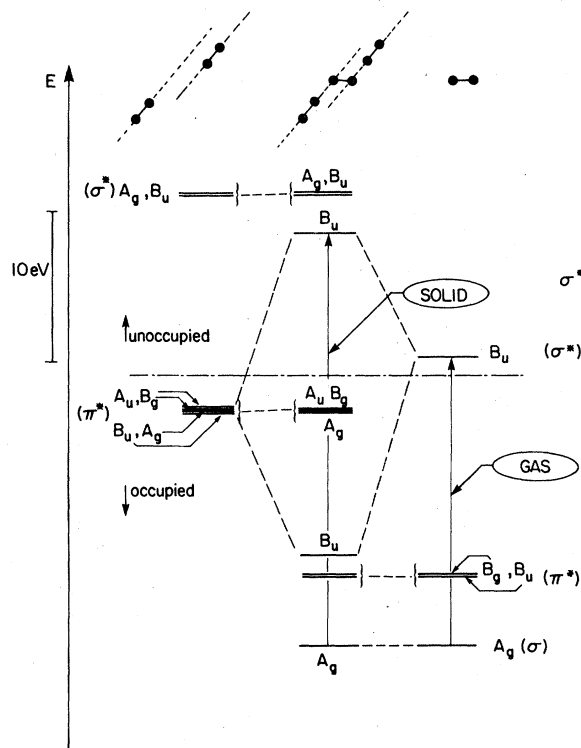


FIG. 7. Molecular interaction diagram to simulate the I_2 intermolecular interactions in the solid phase is shown. The rationale is explained in the text.

elements given by²⁴

$$I_k \propto |\langle \psi_i^{N-1} | a_k | \psi_0^N \rangle|^2, \quad (2)$$

where ψ_i^{N-1} is the final state of the ion, ψ_0^N is the ground state of the neutral molecule, and a_k is the electron annihilation operator that creates a hole in the k^{th} one-electron orbital. Selection rules are dictated by these matrix elements. Namely, the symmetry of the primary hole-state $a_k | \psi_0^N \rangle$ must be the same as the symmetry of $|\psi_i^{N-1}\rangle$. Table II contains the symmetry states for the halogen molecule with a hole in the s , p , or d core levels, and for the low-energy excited states of a halogen molecule. We have used symbols within an LS coupling scheme, so that a comparison can be made easily with similar tabulations of results on diatomics composed of first row elements. A heavy molecule like iodine would normally be classified using the jj coupling nomenclature. In Table II, rows correspond to valence excitations while columns indicate the primary hole states to which a given valence excitation is to be coupled. The entries in the matrix are the symmetries (and numbers in parentheses) of states that result from the coupling. The selection rule implicit in Eq. (2) can now be applied, that is, the symmetry of the state resulting from the coupling must be identical to that of the primary hole state. For example, with a primary hole in an s state of I_2 , the two s functions are symmetrized to form bonding (g) and antibonding (u) combinations. For core states, the energy separation is estimated⁴¹ to be on the order of 0.01 eV,⁴² not resolvable within our present XPS resolution of about 1 eV. Thus the state is classified with both parities (g and u). The selection rule states that the integral implicit in Eq. (2) is nonzero only if both $a_k | \psi_0^N \rangle$ and $|\psi_i^{N-1}\rangle$ have the same symmetry.

Thus, the $^2\Sigma_{g,u}$ column under the s hole (primary hole) contains a $\Sigma_{g,u}$ entry only in the $\sigma^* \leftarrow \sigma$ row (i.e., the $1,^3\Sigma_u$ row). Thus only $\sigma^* \leftarrow \sigma$ transitions couple to the core hole in an s state in I_2 . In the case of a primary core hole in a p state, the situation changes. Under the p -hole entry in Table II are two columns, one for $^2\Sigma_{g,u}$ and one for $^2\Pi_{g,u}$, since p functions transform as either Σ or Π . Still, only $\sigma^* \leftarrow \sigma$ transitions couple, i.e., under the $^2\Sigma_{g,u}$ column another Σ is found only in the $\sigma^* \leftarrow \sigma$ row, and under the $^2\Pi_{g,u}$ column, another Π is found only in the $\sigma^* \leftarrow \sigma$ row. The coupling of a primary hole, of $^2\Pi_{g,u}$ symmetry, to the $\sigma^* \leftarrow \pi$ excitations, however, leads to Σ symmetry. Through an interaction of these states, $\pi^* \leftarrow \sigma$ excitations can be observed. The intensities of these $\pi^* \leftarrow \sigma$ excitations should be weaker than the $\sigma^* \leftarrow \sigma$ excitations, however, since they derive their intensity through a secondary coupling mechanism. A similar argument holds for d holes.

Experimentally, these selection rules can be verified by combining the information available from our study with the high-resolution spectra obtained by Gelius.⁷ Our measurements show that the intense shake-up at about 10 eV is present in all of the core-ionization spectra except for the $4p$ level, where the well-known super Coster-Kronig effects dominate.^{6,7} Our data show that ionization of the $4s$ core level does not result in the shoulder at the 4.9-eV excitation energy. This experimental result is confirmed by the spectra of Gelius,⁷ who does not report the shake-up structure but does show the main line, in which no 4.5-eV shoulder (or peak) appears. The lack of appearance of a 4.5-eV satellite on the $4s$ core-hole peak verifies the selection rule illustrated in Table II.

TABLE II. Symmetries of low-energy excitations in I_2^+ .

Valence excitation		Primary hole					
		s	p	p	d	d	d
Excitation	symmetry	$2+\Sigma_{g,u}$	$2+\Sigma_{g,u}$	$2+\Sigma_{g,u}$	$2\Pi_{g,u}$	$2\Pi_{g,u}$	$2\Delta_{g,u}$
$\sigma^* \leftarrow \pi$	$1,^3\Pi_u$	$(2)2,4\Pi_{g,u}$	$(2)2,4\Pi_{g,u}^+$	$(2)2,4\Sigma_{g,u}^+$	$(2)2,4\Pi_{g,u}$	$(2)2,4\Sigma_{g,u}^+$	$(2)2,4\Pi_{g,u}$
$\sigma_g^2 \pi_u^4 \pi_g^3 \sigma_u^1$				$(2)2,4\Sigma_{g,u}^-$		$(2)2,4\Sigma_{g,u}^-$	$(2)2,4\Phi_{g,u}$
				$(2)2,4\Delta_{g,u}$		$(2)2,4\Delta_{g,u}$	
$\sigma^* \leftarrow \sigma$	$1,^3\Sigma_u$	$(2)2,4\Sigma_{g,u}^+$	$(2)2,4\Sigma_{g,u}^+$	$(2)2,4\Pi_{g,u}$	$(2)2,4\Sigma_{g,u}^+$	$(2)2,4\Pi_{g,u}$	$(2)2,4\Delta_{g,u}$
$\sigma_g^1 \pi_u^4 \pi_g^4 \sigma_u^1$							

V. SUMMARY AND CONCLUSIONS

X-ray photoelectron spectra of I_2 molecules in the gas and condensed-molecular solid phases exhibit dramatic differences because the dynamics of the photoionization event induce strong intermolecular interactions in the solid. In the gas-phase spectra, two strong shake-up peaks are observed, at about 10 and 24 eV. These peaks are due to $\sigma^* \leftarrow \sigma$ excitations. In the solid phase, the 24-eV transition disappears, because the final state is a molecular Rydberg state. The 10-eV peak shifts to 18 eV, due to the interaction of the primary core-hole state of the photoionized molecule with the electronic states of neighboring I_2 molecules. The magnitude of this shift is due to the dynamics of the photoemission

measurement. The 30-eV peak in the solid-state spectra is due to double ionizations of the I_2 molecule, shake-off processes, as determined by analysis of previously published Auger spectra. The shake-off intensity is small enough that the 30-eV peak is not observed with our equipment when working with weak signals in the gas phase.

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- ⁴²It should be emphasized that such linear combinations exist even if the hole is localized (Ref. 41).